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# ANTHRAQUINONE AND ANTHRONE SERIES

## Part V. Chlorinated 6-Aminoanthraquinoneacridones

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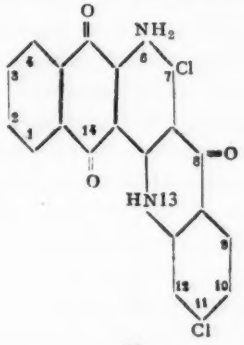
Indanthrene Turquoise Blue GK and 3GK[1] are two vat dyes of the anthraquinone series, marketed by the I. G., which give turquoise blue shades with high fastness to light (7–8) and washing (4–5), but moderate fastness to chlorine (3) and soda boil (3). Both the dyes are dyed in the cold, but are distinguished from other dyes of the IK class in that they are applied from a long liquor (1 : 30) without the addition of common salt and the dyeings are oxidised in water, since the usual air oxidation gives redder and bluer shades.

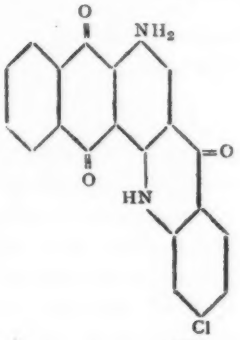
Rowe[2] has described Indanthrene Turquoise Blue GK and 3GK as aminoanthraquinoneacridones such as (I). The trivial name anthraquinoneacridone is used in this paper for the ring system (I) and the substituents are numbered as indicated. Indanthrene Turquoise Blue GK has been recently stated to be 6-amino-11-chloroanthraquinoneacridone (II).[3]



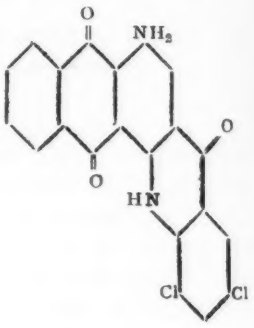

(I)

Elementary analysis of purified and crystallized Indanthrene Turquoise Blue GK indicated the presence of only one atom of chlorine, corresponding to the molecular formula $C_{21}H_{11}O_3N_2Cl$. Analysis of Indanthrene Turquoise Blue 3GK indicated the presence of two chlorine atoms and the molecular formula $C_{21}H_{10}O_3N_2Cl_2$. The present work deals with the syntheses of chloroaminoanthraquinoneacridones, firstly to determine the

constitution of Indanthrene Turquoise Blue GK and 3GK and secondly with a view to examine these compounds as vat dyes. Indanthrene Turquoise Blue GK and 3GK have now been shown to be 11-chloro-6-amino-



(II)



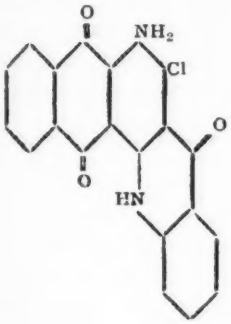
(III)

anthraquinoneacridone (II) and 10: 12-dichloro-6-aminoanthraquinoneacridone (III) respectively.

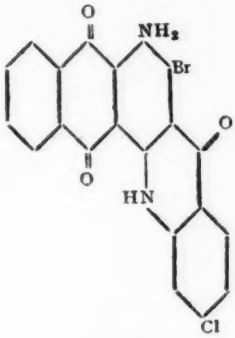
The general method for the synthesis of anthraquinoneacridones consists in the removal of a molecule of water from arylaminoanthraquinones in which there is an *ortho* carboxyl group, which may be present in the anthraquinone or in the aryl half. The cyclization of the intermediate carboxylic acids to the acridones can be brought about by treatment with concentrated sulphuric acid[4] or with chlorosulphonic acid[5] or by conversion of the carboxylic acid to the acid chloride and subsequent treatment with aluminium chloride.[6] Aminoanthraquinoneacridones can be synthesized by the condensation of 4-bromo-1-aminoanthraquinone-2-sulphonic acid with anthranilic acid in aqueous solution in the presence of copper bronze or copper salts and sodium carbonate, the cyclization of the acid and the removal of the sulphonic group being effected simultaneously by treatment of the condensation product with chlorosulphonic acid or fuming sulphuric acid.[7] Alternatively, 4-chloro-1-aminoanthraquinone or 2: 4-dihalogeno-1-aminoanthraquinone can be condensed with anthranilic acid or its halogeno derivatives and the resulting intermediate acid cyclized to the desired acridone by means of sulphuric acid or chlorosulphonic acid.

The synthesis of monochloroaminoanthraquinoneacridones in which the chlorine atom is either in the anthraquinone or in the benzene half of the molecule was first undertaken. Condensation of 2: 4-dichloro-1- aminoanthraquinone[8] with anthranilic acid gave N-1′-(3′-chloro-4′-amino)-anthraquinonylanthranilic acid which was cyclized by means of chlorosulphonic acid

to 7-chloro-6-aminoanthraquinoneacridone (IV). Attempts to cyclize the carboxylic acid with sulphuric acid led to sulphonated products. The dye (IV) gave a greener shade on cotton than Indanthrene Turquoise Blue GK. Another distinction between the two dyes was the facile dehalogenation of (IV) to 6-aminoanthraquinoneacridone by treatment with caustic soda and sodium hydrosulphite at room temperature (29-30°) for an hour; under similar conditions Indanthrene Turquoise Blue GK was unaffected. The dye (IV) can, however, be applied to cotton by the cold-dyeing or




(IV)




(V)

IK process without danger of dehalogenation, if dyeing is commenced immediately after vatting. It has been noticed that 3:3′-dichloro-4:4′-diaminoindanthrone (Indanthrene Green 2B; Caledon Green 2B; Colour Index No. 1116) also undergoes dehalogenation by treatment with aqueous sodium hydroxide and hydrosulphite at 65-70°, but it is applicable by the hot-dyeing or IN process and continues to be in the commercial range of vat colours. A detailed examination of dehalogenation in the anthraquinone series will be reported later.

The parent aminoanthraquinoneacridone was prepared by a second route by condensing anthranilic acid with 4-chloro-1-aminoanthraquinone and subsequent cyclization of N-1′-(4′-amino)-anthraquinonylanthranilic acid by means of chlorosulphonic acid; the acridone can also be prepared from leuco-1:4-diaminoanthraquinone and *o*-chlorobenzoic acid,[9] or by condensing 1:4-dichloroanthraquinone with anthranilic acid, cyclizing and replacing the chlorine atom by the amino group through the *p*-toluenesulphonamide.[10]

Monochloroanthraquinoneacridones having a chlorine atom in the benzene half of the molecule were then synthesized. 5-Chloroanthranilic acid, prepared by the chlorination of anthranilic acid with sulphuryl chloride

in the presence of anhydrous sodium acetate in carbon tetrachloride, was condensed with 4-chloro-1-aminoanthraquinone and the intermediate carboxylic acid was cyclized by sulphuric acid to 10-chloro-6-aminoanthraquinoneacridone. This dyed a greener shade than Indanthrene Turquoise Blue GK. The absorption spectra of the two dyes were also found to be different (Fig. 1). 4-Chloroanthranilic acid, prepared by oxidation of 4-chloro-N-acetyl-*o*-toluidine and subsequent deacetylation,[11] was condensed with 4-chloro-1-aminoanthraquinone and the product obtained was cyclized to give (II). The acridone (II) was found to be identical in all respects with pure Indanthrene Turquoise Blue GK. It was also prepared by condensing 1 : 4-diaminoanthraquinone with 2 : 4-dichlorobenzoic acid and cyclization of the intermediate acid. The absorption spectra of the

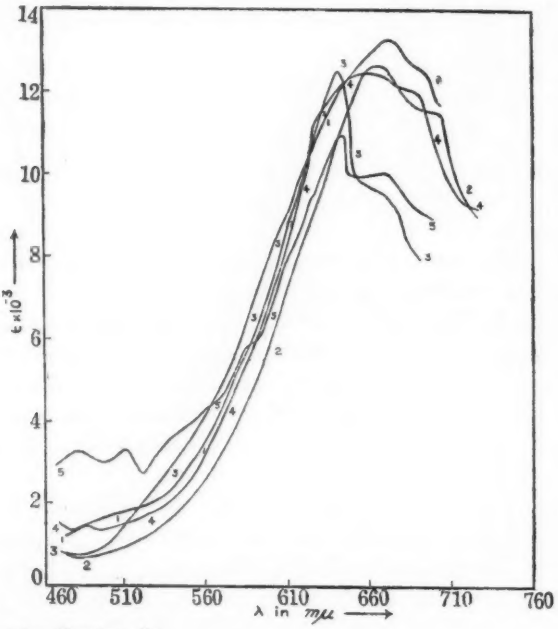



Fig. 1. Absorption Spectra of :

1. 6-Aminoanthraquinoneacridone
2. 10-Chloro-6-aminoanthraquinoneacridone
3. Indanthrene Turquoise Blue GK and 11-Chloro-6-aminoanthraquinoneacridone
4. Indanthrene Turquoise Blue 3 GK and 10 : 12-dichloro-6-aminoanthraquinoneacridone
5. 7-Chloro-6-aminoanthraquinoneacridone

Solvent — quinoline.

synthetic dye (II) and of Indanthrene Turquoise Blue GK in quinoline in the visible range also showed their complete identity (Fig. 1).

The stability of both the chlorine atoms in Indanthrene Turquoise Blue 3GK to treatment with sodium hydroxide and hydrosulphite under the usual dyeing conditions indicated that there is no chlorine atom adjacent to the amino group in the anthraquinone nucleus as in (IV) and probably that both of these are in the benzene half of the anthraquinoneacridone. 3:5-Dichloroanthranilic acid[12] was condensed with 4-chloro-1-aminoanthraquinone and the intermediate N-1'-(4'-amino)-anthraquinonyl-3:5-dichloroanthranilic acid was cyclized with sulphuric acid to (III). This dye and pure Indanthrene Turquoise Blue 3GK were found to be identical in crystalline form, colour of the vat, shade on cotton yarn and colour reactions. The absorption spectra in the visible range of the synthetic dye (III) and pure Indanthrene Turquoise Blue 3GK were also identical (Fig. 1). The dye (III) was also synthesized by an alternative route starting from 4-bromo-1-aminoanthraquinone-2-sulphonic acid and 3:5-dichloroanthranilic acid; the condensation was effected in aqueous solution and the product was cyclized and desulphonated. 7:11-Dichloro- and 7:10-dichloro-6-aminoanthraquinoneacridones, isomers of (III), containing one chlorine atom in the anthraquinone half, were also synthesized, starting from 2:4-dichloro-1-aminoanthraquinone and 4-chloro- and 5-chloroanthranilic acid respectively. The dyes gave shades on cotton which were different from those given by Indanthrene Turquoise Blue 3GK and which had good fastness properties (light 7, chlorine 3-4, soda boil 3-4; and light 7-8, chlorine 3, soda boil 2-3 respectively). Indanthrene Blue 8GK, which is apparently not marketed at the present time, has been stated to be 7:10-dichloro-6-aminoanthraquinoneacridone.[13]

7:10:12-Trichloro-6-aminoanthraquinoneacridone, prepared from 2:4-dichloro-1-aminoanthraquinone and 3:5-dichloroanthranilic acid, gave a greenish blue shade possessing good fastness to light (7) and moderate fastness to chlorine (3) and soda boil (4). When this trichloro compound was treated with aqueous sodium hydroxide and hydrosulphite at 30° for one hour, the product on crystallization contained only two chlorine atoms and was identical with Indanthrene Turquoise Blue 3GK. A dihalogenoaminoanthraquinoneacridone having a bromine atom in the anthraquinone nucleus and a chlorine in the benzene half (V) was synthesized in the usual manner by the condensation of 2:4-dibromo-1-aminoanthraquinone with 4-chloroanthranilic acid. It dyed cotton green-blue shade from a red-brown vat.

## Experimental

*Purification of Indanthrene Turquoise Blue GK*:

The commercial dye (paste) (50 g.) was boiled with 5% hydrochloric acid (200 c.c.) for one hour and filtered. The residue (8 g.) crystallized from nitrobenzene in blue needles (Found: N, 7·1; Cl, 9·4. $C_{21}H_{11}O_3N_2Cl$ requires N, 7·4; Cl, 9·5%). The blue shade on cotton (I.K. process) has light fastness 7, chlorine 3, and soda boil 2–3. The vat is brown-violet in colour.

*Purification of Indanthrene Turquoise Blue 3GK* (powder fine for dyeing):

The commercial dye (5 g.) was boiled with 5% hydrochloric acid (100 c.c.) for one hour. After allowing the mixture to settle for two days, the acid extract was decanted off and the dye was isolated by centrifuging the suspension and washed. The purified dye (2·7 g.) crystallized from boiling nitrobenzene as long blue needles (Found; C, 61·5; H, 2·1; N, 7·3; Cl, 16·9. $C_{21}H_{10}O_3N_2Cl_2$ requires C, 61·6; H, 2·4; N, 6·9; Cl, 17·2%). The pure dye dyes a turquoise blue shade on cotton from a brown-violet vat (fastness to light 7; chlorine 3–4; soda boil 3).

5-*Chloroanthranilic acid*:

Anthranilic acid (1·37 g.) and anhydrous sodium acetate (0·9 g.) were suspended in carbon tetrachloride (20 c.c.) and a solution of sulphuryl chloride (1·49 g.; 1·1 mol.) in carbon tetrachloride (2 c.c.) was added slowly under stirring. After 3 hours, the suspension was filtered, the residue suspended in water and neutralised by the addition of sodium acetate. The crude 5-chloroanthranilic acid (1·3 g.), m.p. 205°, crystallized from alcohol in needles, m.p. 211–2° (Found: Cl, 20·5. Calc. for $C_7H_6O_2NCl$: Cl, 20·7%).

7-*Chloro*-6-*aminoanthraquinoneacridone* (IV):

2:4-Dichloro-1-aminoanthraquinone (2·92 g.), anthranilic acid (2·05 g.) anhydrous potassium acetate (1·96 g.) and copper bronze (0·06 g.) were refluxed under stirring with amyl alcohol (20 c.c.) for 8 hours. The blue mass was filtered hot, washed with alcohol, boiled with dilute hydrochloric acid (100 c.c.) for 30 minutes, filtered and washed. On crystallization from glacial acetic acid, N-1′-(3′-chloro-4′-amino)-anthraquinonylanthranilic acid was obtained as long blue needles (3·4 g.), m.p. 291–2° (Found: N, 6·9; Cl, 8·9. $C_{21}H_{13}O_4N_2Cl$ requires N, 7·1; Cl, 9·0%). It dissolves in alcoholic ammonia giving a blue solution. On treating the carboxylic acid with concentrated sulphuric acid at 98–100° or with 20% fuming sulphuric acid at room temperature, a water-soluble sulphonic acid was obtained.

The carboxylic acid (1·5 g.) was dissolved in chlorosulphonic acid (12·7 c.c.); after keeping in a stoppered flask for 24 hours, the red-brown solution was poured into a porcelain dish and allowed to stand in moist air for 10 days, when a red-violet product separated. This was filtered, and washed with hot alcohol until the washings were colourless. The residue (1·0 g.) crystallized from nitrobenzene in blue plates. The dye (IV) does not melt up to 360° (Found: N, 7·4; Cl, 9·4. $C_{21}H_{11}O_3N_2Cl$ requires N, 7·4; Cl, 9·5%). The vat is red-brown in colour and the green-blue shade on cotton has fastness grades of light 7, chlorine 3, and soda boil 2.

10-*Chloro*-6-*aminoanthraquinoneacridone*:

4-Chloro-1-aminoanthraquinone (2·4 g.), 5-chloroanthranilic acid (7·1 g.), anhydrous sodium acetate (1·0 g.), copper bronze (0·05 g.), anhydrous copper sulphate (0·1 g.) and amyl alcohol (40 c.c.) were heated at 140° for 24 hours. After removal of the solvent by steam-distillation, the product was filtered off and washed successively with sodium carbonate solution and hot dilute hydrochloric acid. N-1′-(4′-Amino)-anthraquinonyl-5-chloroanthranilic acid crystallized from glacial acetic acid in blue needles (2·1 g.), m.p. 265–6° (Found: Cl, 9·0. $C_{21}H_{13}O_4N_2Cl$ requires Cl, 9·0%). The above acid (1·02 g.), boric acid (0·05 g.) and concentrated sulphuric acid (12 c.c.) were heated at 150° for 15 minutes. The resultant acridone was isolated (0·6 g.) and it crystallized from nitrobenzene in blue needles which did not melt up to 360° (Found: N, 7·6; Cl, 9·3. $C_{21}H_{11}O_3N_2Cl$ requires N, 7·4; Cl, 9·5%). The fastness grades of the blue-green shade on cotton were light 7, chlorine 3, and soda boil 3.

6-*Aminoanthraquinoneacridone*:

4-Chloro-1-aminoanthraquinone (2·58 g.), anthranilic acid (6·8 g.), anhydrous sodium acetate (1·0 g.), copper bronze (0·1 g.), anhydrous copper sulphate (50 mg.) and amyl alcohol (40 c.c.) were refluxed for 24 hours. Amyl alcohol was removed by steam-distillation and the residue was washed with hot sodium carbonate and dilute hydrochloric acid, and dried (3·7 g.). Crystallization from glacial acetic acid gave N-1′-(4′-amino)-anthraquinonylanthranilic acid in blue needles, m.p. 263° (Found: N, 7·4. $C_{21}H_{14}O_4N_2$ requires N, 7·8%). The acid (0·5 g.) was dissolved in chlorosulphonic acid (6·0 c.c.) and the solution warmed to 35–40° for 5 minutes. The red-brown solution was poured on crushed ice, and the blue precipitate collected (0·4 g.). The acridone crystallized from nitrobenzene in plates (Found: N, 8·3. Calc. for $C_{21}H_{12}O_3N_2$: N, 8·2%). The dye gives a light blue shade on cotton from a brown vat (fastness to light 6, chlorine 3, soda boil 2).

11-*Chloro*-6-*aminoanthraquinoneacridone* (*II*):

(*a*) 4-Chloro-1-aminoanthraquinone (1·2 g.), 4-chloroanthranilic acid (0·9 g.), anhydrous copper sulphate (0·1 g.), copper bronze (20 mg.), anhydrous sodium acetate (0·8 g.) and amyl alcohol (40 c.c.) were refluxed for 24 hours and N-1′-(4′-amino)-anthraquinonyl-4-chloroanthranilic acid was isolated as usual and crystallized in blue needles from acetic acid (Found: Cl, 8·9. $C_{21}H_{13}O_4N_2Cl$ requires Cl, 9·0%).

The acid (0·5 g.) was treated with concentrated sulphuric acid (5 c.c.) at 98° for 20 minutes, during which the colour of the solution changed from blue to bottle green. On cooling and pouring on ice, the product (II; 0·3 g.) was obtained which crystallized from nitrobenzene in blue needles (Found: N, 7·4; Cl, 9·3. $C_{21}H_{11}O_3N_2Cl$ requires N, 7·4; Cl, 9·5%). The above dye and pure Indanthrene Turquoise Blue GK showed identical dyeing properties and colour reactions.[14]

(*b*) Sublimed 1: 4-diaminoanthraquinone (2·38 g.; 1 mol.), potassium 2: 4-dichlorobenzoate (2·3 g.; 1 mol.), anhydrous sodium acetate (2·0 g.), anhydrous copper sulphate (0·5 g.), copper bronze (20 mg.) and nitrobenzene (40 c.c.) were refluxed for 24 hours at 230°. Nitrobenzene was steam-distilled, the residue filtered, washed with dilute hydrochloric acid and 10% sodium carbonate solution, and extracted with ammonia. The blue solution was acidified with hydrochloric acid and the precipitate of N-1′-(4′-amino)-anthraquinonyl-4-chloroanthranilic acid was washed and dried (0·7 g.). The acid was cyclized as above and the acridone (II) crystallized from nitrobenzene (Found: N, 7·4%).

10: 12-*Dichloro*-6-*aminoanthraquinoneacridone* (*III*):

(*a*) 4-Chloro-1-aminoanthraquinone (2·57 g.), 3: 5-dichloroanthranilic acid (3·0 g.), anhydrous sodium acetate (1·0 g.), copper bronze (20 mg.), anhydrous copper sulphate (0·05 g.) and amyl alcohol (35 c.c.) were refluxed at 150° for 28 hours. Isolated as usual, N-1′-(4′-amino)-anthraquinonyl-3: 5-dichloroanthranilic acid (2·0 g.) crystallized from acetic acid in blue needles, m.p. 280° (Found: N, 6·7. $C_{21}H_{12}O_4N_2Cl_2$ requires N, 6·5%). The acid (0·2 g.) was heated with concentrated sulphuric acid (2 c.c.) at 98–100° for 20 minutes and the acridone (III; 0·18 g.) crystallized from nitrobenzene in long blue needles which did not melt up to 400° (Found N: 6·9; Cl, 16·9. $C_{21}H_{10}O_3N_2Cl_2$ requires N, 6·9; Cl. 17·2%). The dye (III) was identical in all properties with purified Indanthrene Turquoise Blue 3GK.

(*b*) 4-Bromo-1-aminoanthraquinone-2-sulphonic acid (2·02 g.), 3: 5-dichloroanthranilic acid (1·12 g.), anhydrous potassium carbonate

(0·8 g.), copper bronze (0·5 g.) and water (25 c.c.) were heated together at 95° for 6 hours. The blue mass was diluted with water (100 c.c.), acidified with hydrochloric acid, heated to 80° for 30 minutes and filtered hot. The residue was washed with water till the washings were pink in colour and dried (2·0 g.). The N-1′-(4′-amino-3′-sulpho)-anthraquinonyl-3: 5-dichloroanthranilic acid (0·5 g.) thus obtained was added slowly to chlorosulphonic acid (2 c.c.) at 35°. After two hours the mixture was poured into crushed ice and the blue precipitate collected (0·25 g.) and washed with hot water. Crystallization from nitrobenzene gave (III) in blue needles (Found: C, 61·5; H, 2·5; N, 6·8. $C_{21}H_{10}O_3N_2Cl_2$ requires C, 61·6; H, 2·4; N, 6·9%), which were identical with purified and crystallized Indanthrene Turquoise Blue 3GK.

7: 11-*Dichloro-6-aminoanthraquinoneacridone*:

2: 4-Dichloro-1-aminoanthraquinone (2·92 g.), 4-chloroanthranilic acid (2·74 g.), copper bronze (0·05 g.), copper acetate (20 mg.), anhydrous potassium acetate (1·96 g.) and amyl alcohol (20 c.c.) were refluxed for 15 hours with stirring. The mixture was filtered, washed repeatedly with hot methylated spirit, 10% sodium carbonate and dilute hydrochloric acid. The crude N-1′-(3′-chloro-4′-amino)-anthraquinonyl-4-chloroanthranilic acid (3·0 g.) crystallized from nitrobenzene in blue needles, m.p. 310-11° (Found N, 6·3. $C_{21}H_{12}O_4N_2Cl_2$ requires N, 6·5%). The acridone crystallized in blue needles from nitrobenzene (Found: N, 6·6; Cl, 17·0. $C_{21}H_{10}O_3N_2Cl_2$ requires N, 6·9; Cl, 17·2%). It dyes a blue green shade on cotton from a brown vat (fastness to light 7, chlorine 3-4, and soda boil 3-4).

7: 10-*Dichloro-6-aminoanthraquinoneacridone*:

Prepared as usual from 2: 4-dichloro-1-aminoanthraquinone and 5-chloroanthranilic acid, the intermediate N-anthraquinonylanthranilic acid crystallized from nitrobenzene in blue needles, m.p. 308-9° (Found: Cl, 16·4. $C_{21}H_{12}O_4N_2Cl_2$ requires Cl, 16·6%). The acridone crystallized from *o*-dichlorobenzene in blue needles (Found: N, 7.0; Cl, 17·0. $C_{21}H_{10}O_3N_2Cl_2$ requires N, 6·9; Cl, 17·2%). The turquoise blue shade on cotton is greener than the shade from Indanthrene Turquoise Blue 3GK (fastness to light 7-8, chlorine 3, and soda boil 2-3).

7: 10: 12-*Trichloro-6-aminoanthraquinoneacridone*:

The condensation product of 2: 4-dichloro-1-aminoanthraquinone and 3: 5-dichloroanthranilic acid crystallized from glacial acetic acid in long blue needles, m.p. 267-8° (Found N, 5·8. $C_{21}H_{11}O_4N_2Cl_3$ requires N, 6·0%).

The acridone crystallized from *o*-dichlorobenzene in long blue needles not melting up to 370° (Found: N, 6·3; Cl, 23·8. $C_{21}H_9O_3N_2Cl_3$ requires N, 6·3; Cl, 24·0%). The product dyes a bright green-blue shade from a violet brown vat (fastness to light 7, chlorine 3, and soda boil 4).

11-*Chloro-7-bromo-6-aminoanthraquinoneacridone* (*V*):

2:4-Dibromo-1-aminoanthraquinone (1·9 g.), 4-chloroanthranilic acid (0·85 g.), anhydrous sodium acetate (0·8 g.), copper bronze (0·3 g.), and amyl alcohol (35 c.c.) were refluxed for 14 hours. The product was worked up as usual. N-1-(3′-Bromo-4′-amino) anthraquinonyl-4-chloroanthranilic acid (2·2 g.) crystallized from glacial acetic acid in blue needles, m.p. 285° (Found N, 5·6; Cl+Br, 24·2. $C_{21}H_{12}O_4N_2ClBr$ requires N, 5·9; Cl+Br, 24·4%). The acridone (V) cristallized from *o*-dichlorobenzene in long blue needles, which did not melt up to 360° (Found: N, 5·8. $C_{21}H_{10}O_3N_2ClBr$ requires N, 6·1%). The green-blue shade on cotton from a red-brown vat has fastness to light 7-8, chlorine 3, and soda boil 2-3.

*Dechlorination of 7-chloro-6-aminoanthraquinoneacridone by aqueous sodium hydroxide and hydrosulphite*:

The chloroacridone (0·18 g.) was pasted with a little Turkey Red Oil, 10% sodium hydroxide (5 c.c.) and hydrosulphite (0·5 g.) were added, and the solution was diluted to 50 c.c. The violet-brown vat was kept under alkaline and reduced condition at 28° (room temperature) for one hour, after which it was oxidised by passing air. The finely divided blue precipitate was centrifuged, repeatedly washed with water and dried (0·14 g.). The product did not contain chlorine, and crystallized from nitrobenzene, in blue plates (Found: N, 8·3. Calc. for $C_{21}H_{12}O_3N_2$: N, 8·2%). It dyes a blue shade on cotton which is identical with the shade of 6-aminoanthraquinoneacridone, and is different from the shade of the original chloroacridone.

Indanthrene Turquoise Blue GK and 3GK, when treated as described above, remained unaffected and gave their original shades on dyeing. (Indanthrene Turquoise Blue GK:—Found: Cl, 9·2. $C_{21}H_{11}O_3N_2Cl$ requires Cl, 9·5%) (Indanthrene Turquoise Blue 3GK:—Found: Cl, 16·8. $C_{21}H_{10}O_3N_2Cl_2$ requires Cl, 17·2%).

7:10:12-Trichloro-6-aminoanthraquinoneacridone gave 10:12-dichloro-6-aminoanthraquinoneacridone (Indanthrene Turquoise Blue 3GK) by treatment with alkali and hydrosulphite at room temperature for one hour (Found: N, 6·9; Cl, 16·9. $C_{21}H_{10}O_3N_2Cl_2$ requires N, 6·9; Cl, 17·2%).

## Summary

Indanthrene Turquoise Blue GK and 3GK have been shown to be 11-chloro-6-aminoanthraquinoneacridone (II) and 10: 12-dichloro-6-aminoanthraquinoneacridone (III) respectively by unambiguous synthesis. The absorption spectra of the commercial and the synthetic dyestuffs have been determined. Chloro derivatives of 6-aminoanthraquinoneacridone, substituted by chlorine in the anthraquinone nucleus, in the benzene half of the molecule, and in both the anthraquinone and the benzene halves, have been synthesised, and the fastness properties of the shades on cotton determined. 6-Aminoanthraquinoneacridone has been prepared by a new route; the various chloro derivatives of 6-aminoanthraquinoneacridone which have been synthesised are the 7-, 10-, and 11-monochloro, 7: 10-, 7: 11- and 10: 12-dichloro, the 7: 10: 12-trichloro and 11-chloro-7-bromo-compounds. It is found that the acridones containing a chlorine atom in the 7-position, adjacent to the amino group, are dehalogenated by treatment with aqueous alkali and hydrosulphite at room temparature (28°) for about one hour.


We are indebted to the Council of Scientific and Industrial Research under whose auspices the work was carried out, and to Mr. T. S. Gore for the microanalyses recorded in the paper.

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# STUDIES IN OXYCELLULOSE

## Part III. Oxidation of Cellulose with a Mixture of Nitrogen Dioxide and Oxygen

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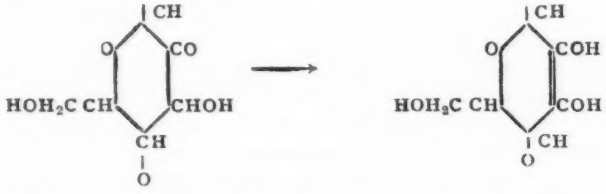
### Introduction

Kenyon and co-workers[1–4] have studied the oxidation of cellulose with nitrogen dioxide at room temperature (21° C.), and their conclusions may be summarised as follows:

(i) Nitrogen dioxide oxidises cellulose to give highly acidic products—designated celluronic acids—which dissolve in dilute alkali when the carboxyl content is 13·5% or more as determined by the carbon dioxide evolution method.

(ii) Nitrogen dioxide preferentially converts the primary alcoholic groups to carboxyl and is said to leave the glucosidic linkages unaffected.

In one of their communications they have described an investigation of the oxidation of cellulose by nitrogen dioxide dissolved in carbon tetrachloride and have suggested a mechanism of oxidation of cellulose.[3] In their latest contribution[4] to this subject, Kenyon and co-workers have examined the alkali lability of celluronic acids and have concluded that to a certain extent a secondary alcoholic group is oxidised to a keto group which in presence of alkali gives rise to an ene-diol thus:




Evidence in favour of Kenyon's conclusions has been supplied by Head[5] and by Rowen, Hunt and Plyer.[6]

Examination of the literature reveals that no work has been carried out on the oxidation of cellulose by a mixture of nitrogen dioxide and oxygen

except for a paper,[7] which is available to the authors only in the form of an abstract. In this abstract it has been stated that the oxidation of cellulose by oxygen is catalysed by nitrogen dioxide. The present investigation has been undertaken with a view to elucidate the mechanism of oxidation of cellulose by a mixture of nitrogen dioxide and oxygen, since it is felt that this would be distinctly different from the one postulated by Kenyon and collaborators referred to above.

A number of oxycelluloses have been prepared using nitrogen dioxide alone and in admixture with oxygen as oxidants. A few samples of periodic acid and dichromate oxalic acid oxycelluloses were also prepared. Their properties such as copper number, carboxyl content, cuprammonium fluidity, effect of alkali treatment on copper number, etc., have been studied before and after treatment of the oxycelluloses with chlorous acid.

## General Details of Experimental Methods

### *Materials*

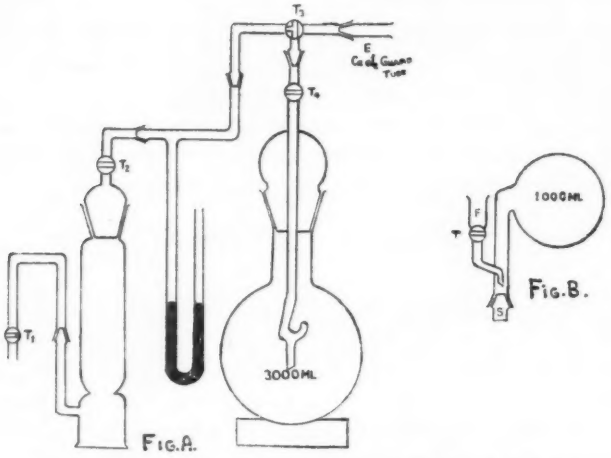
*Cotton.*—The material used for oxidation is carefully purified and bleached 18's yarn made from Indian cotton. In the preliminary experiment the material has been oxidised in the form of hanks. Later, for convenience of manipulation, oxidations have been carried out with the above yarn cut into 1″ lengths. In all experiments the cotton cellulose is dried at 105-10° C. for 2 hours and cooled in a desiccator.

*Liquid nitrogen dioxide.*—The gases evolved by the action of a mixture of one part conc. sulphuric acid and four parts of fuming nitric acid on anhydrous sodium nitrite are dried by passage over fused calcium nitrate and phosphorous pentoxide and condensed in a receiver cooled in a freezing mixture. The gases condense to a deep green liquid which is oxidised by bubbling dry oxygen. The oxidation is considered to be complete when the liquid no longer possessess any greenish tint. The liquid which is bright orange in colour, is stored in oxygen atmosphere under slight pressure for at least 48 hours. Prior to use the liquid is distilled over phosphorous pentoxide and condensed in a receiver cooled by immersion in crushed ice. During the preparation, storage and distillation the nitrogen dioxide is protected against atmospheric moisture by means of calcium chloride guard tubes.

The nitrogen dioxide prepared as described is used in (*a*) gaseous form, (*b*) in solution in freshly distilled dry carbon tetrachloride and (*c*) in admixture with oxygen for oxidation of cellulose.

*Details of apparatus used for oxidation.*—For oxidation of cotton cellulose with a mixture of nitrogen dioxide and oxygen, the arrangement of

apparatus used is shown diagrammatically in Fig. A. Where pure nitrogen dioxide has been used as the oxidant either in gaseous state or as a solution in carbon tetrachloride, the flask shown in Fig. B, is used. In the preliminary experiments the reaction vessel was a 10 l. bottle with a ground-in-stopper carrying a glass hook for suspending the hank. The apparatus is enclosed in an air thermostat maintained at 35° C.




Arrangement of Apparatus used for Oxidation of Cellulose

*The following methods of oxidation have been used*:

*Method A*: *Oxidation of cellulose by a mixture of nitrogen dioxide and oxygen under pressure.*—The various parts of the apparatus are dried in a current of hot air and assembled as shown in Fig. A. Cotton yarn in the form of a hank is suspended from the hook. The drying tower contains fused calcium nitrate as the desiccant.

The assembled apparatus is evacuated through $T_1$ till the manometer registers a vacuum of 25″ of mercury. Then $T_1$, $T_2$, $T_3$ and $T_4$ are closed and the T piece containing the three-way tap $T_3$ is disconnected. A measured volume of freshly distilled liquid nitrogen dioxide is introduced into the upper tube of $T_4$ and the liquid is sucked in by opening $T_4$. As soon as the whole of the liquid is sucked in $T_4$ is closed and the apparatus is again restored to its original assembled position. $T_2$, $T_3$ and $T_4$ are opened, $T_1$ is connected to an oxygen cylinder and oxygen introduced by opening $T_1$. When the requisite pressure is attained, $T_1$, $T_2$, $T_3$ and $T_4$ are closed. The reaction is allowed to proceed for a predetermined time. At the end of the

reaction period the drying tower is disconnected and the residual gases removed by evacuation. The oxycellulose is transferred to a large beaker containing cold distilled water and washed with repeated changes till free from acid. The material is dried carefully at room temperature away from light and dust, conditioned and carefully stored.

*Method B*: *Oxidation of cotton cellulose with a mixture of nitrogen dioxide and oxygen at atmospheric pressure.*—In this case a mixture of nitrogen dioxide and oxygen has been prepared as described above, but the addition of oxygen is stopped as soon as the mixture attains atmospheric pressure. The mixture is allowed to stand overnight after closing $T_2$ and $T_4$. The dried material is then introduced by momentarily removing the ground-in-stopper of the reaction vessel. The stopper is immediately placed in position. At the end of the reaction period the residual gases are removed and the oxycellulose is washed, dried and stored as described earlier.

*Method C*: *Oxidation of cotton cellulose with pure nitrogen dioxide.*—The apparatus shown in Fig. B is used. The flask containing the weighed amount of cotton cellulose is heated at 105–10° C. for two hours and immediately stoppered to prevent contact with moisture. The flask is then evacuated as completely as possible through T using a Hyvac pump. T is then closed, the Hyvac pump is disconnected and a measured volume of freshly distilled anhydrous liquid nitrogen dioxide is poured from a measuring cylinder into the funnel F. The liquid is sucked in by opening T, which is closed as soon as all the liquid has gone in. The liquid falls into the hollow stopper S from which it rapidly evaporates to fill the flask with nitrogen dioxide fumes. The flask is kept in an air-thermostat maintained at 35° C. for the requisite period. At the end of this period, the gases are removed by evacuation and the oxycellulose is washed free from acid, dried and stored as before.

When a solution of nitrogen dioxide in carbon tetrachloride is used as the oxidant the method is modified as follows. A weighed amount of cotton—dried as mentioned earlier—is suspended in a known volume of anhydrous redistilled carbon tetrachloride in the flask shown in Fig. B. It is evacuated till the carbon tetrachloride starts boiling vigorously at 35° C. T is then closed and the pump disconnected. A known amount of freshly distilled dry liquid nitrogen dioxide is introduced as before which collects in the hollow stopper S. The liquid is then dissolved by rapidly inverting and shaking the flask a number of times, so that a homogeneous solution of nitrogen dioxide in carbon tetrachloride is obtained. At the end of the reaction period the oxidised sample is separated from the solution by filtration, washed free from acid, dried and stored as mentioned earlier.

*Periodic acid and dichromate-oxalic acid oxycelluloses.*—These have been prepared and rendered cation-free as described in an earlier communication.[8]

*Treatment of the oxycelluloses with chlorous acid.*—The various oxycelluloses are treated with 0·1 M sodium chlorite in 0·5 M phosphoric acid for 18 hours at room temperature.[9] The samples are then washed, rendered cation free, air-dried and carefully stored.

*Determination of combined nitrogen.*—The nitrogen content of the sample has been estimated by De-varda's method.[10]

*Determination of copper number.*—Due to the high copper number of the oxycellulose samples, a modification of Heyes' method[11, 8] has been used. As in many cases, the sample is completely disintegrated during the copper number determination, the precipitate of cuprous oxide is filtered through a $G_4$ sintered glass crucible instead of the usual $G_3$ grade.

*Determination of copper number after alkali treatment.*—It has been observed during the examination of the alkali solubility of the oxycelluloses produced by method A that their solution in dilute caustic soda (0·25 N) does not give any precipitate on acidification if the solution is kept aside for sufficient time prior to acidification. The same change is effected by heating the alkaline solution on a boiling water-bath for fifteen minutes. Hence it is evident that hydrolysis takes place both during storage and by heating. With a view to examine the effect of alkali treatment on the reducing power of the oxycelluloses the following method has been used.

The sample (0·1 g.) is weighed and transferred to a Pyrex test tube ($6'' \times \frac{3}{4}''$). Caustic soda solution (10 ml. of 0·25 N) is poured over the sample and the sample distributed throughout the solution by means of a thin glass rod. The test tube is heated by immersion in a boiling water-bath for 15 minutes. The mouth of the test tube is closed by means of a pear-shaped glass bulb. At the end of 15 minutes the test tube is cooled in running water and the contents transferred to a 100 ml. Pyrex conical flask. The test tube is rinsed out into the conical flask with 9 ml. of distilled water divided into three lots. The caustic soda is then neutralised by addition of 1 ml. of 2·5 N sulphuric acid. Glucose solution (10 ml. of 0·04% solution) is added to the mixture followed by addition of a boiling mixture of sodium carbonate-bicarbonate solution (75 ml.), copper sulphate solution (5 ml.) and sodium carbonate -bicarbonate mixture (3 : 1 ; 4 g.). The rest of the procedure is as for the usual copper number determination. A blank determination is also carried out without any cotton.

*Determination of carboxylic acid content.*[12]—The carboxylic acid content of the oxycelluloses has been determined by Neale and Stringfellow's Alkali titration method, with suitable modification. The cation-free sample [0·5 g. (0·25 g. if $-COOH > 9\%$)] is suspended in a mixture of 25 ml. of 5% sodium chloride, 25 ml. of N/50 caustic soda (carbonate-free) and 25 ml. of carbon dioxide-free distilled water. At the end of one hour the excess of caustic soda is backtitrated with 0·02 N hydrochloric acid using 0·04% bromocresol purple solution as indicator.

Neale and Stringfellow's method for the determination of the carboxyl content has been criticised strongly by Kenyon,[13] and by Davidson.[9, 14] The latter has shown that it gives fictitious values for highly reducing oxycelluloses. The carboxylic acid content in the above oxycelluloses has also been determined by the Iodometric method developed in this laboratory.[8] This method does not involve the use of alkali. In this method 0·5 g. (0·25 g. if $-COOH$ is more than 9%) of the cation-free sample is suspended in a mixture of 25 ml. of $KIO_3$ : KI : NaCl solution (21·4 g.: 83 g.: 50 g. respectively per litre) and 25 ml. of carbon dioxide-free distilled water. After standing for twenty-four hours the mixture is titrated against 0·02 N iodine using starch solution as indicator. The carboxyl content is expressed as milliequivalents of carboxyl per 100 g. of the dry material.

*Determination of cuprammonium fluidity.*—The cuprammonium hydroxide solution used in the determinations has been prepared according to the method described by Pacsu and Mehta,[15] and the fluidity determinations have been carried out by the method recommended by the B.C.I.R.A.[16]

Due to the highly degraded nature of the oxycelluloses a 1% solution has been used for the determination.

## Experimental Results and Discussion

The chemical properties and behaviour of the nitrogen dioxide + oxygen oxycelluloses prepared as described earlier are summarised in Tables I and II and represented graphically in Figs. 1, 2, 3 and 4.

In Table I are given the results of oxycelluloses obtained by using the oxidant under pressure. From Figs. 1 and 2 it is evident that while carboxyl content by Neale's method increases progressively with the time of oxidation, the copper number increases very rapidly and attains a maximum value at an early stage of oxidation and then remains constant. If the oxycelluloses are treated with alkali prior to copper number determination it is found that the copper number falls to nearly a third of its original value. Oxycelluloses thus obtained are progressively more soluble in dilute caustic soda solu-

TABLE I

*Oxidation of cellulose with a mixture of nitrogen dioxide and oxygen*

| Time of reaction hours | Carboxyl content (Neale's method) milliequivalents per 100 g. of material | Copper number | | | Solubility in alkali | | | | Nitrogen content % |
|---|---|---|---|---|---|---|---|---|---|
| | | Before treatment with alkali | After treatment with alkali | COOH content per cent. | 2% caustic soda | | 1% caustic soda | | |
| | | | | | After 5 minutes | Overnight contact | After 5 minutes | Overnight contact | |
| 4 | 76·6 | 59·51 | 25·02 | 3·45 | ....Insoluble.... | | ....Insoluble.... | | 1·35 |
| 8 | 123·5 | 71·01 | 26·37 | 5·56 | ....50 per cent. soluble.... | | | | .. |
| 16 | 160·3 | 87·25 | 25·36 | 7·20 | ....75 per cent. soluble..... | | | | 1·94 |
| 24 | 177·3 | 86·56 | 25·36 | 7·98 | ....95 per cent. soluble..... | | | | 2·37 |
| 40 | 202·8 | 86·56 | 25·02 | 9·13 | ....completely soluble..... | | | | 1·81 |

Material: 20 g. of bone-dry cotton in 10 l. flask.

Oxidant: 10 ml. of nitrogen dioxide (measured at 0° C.) + oxygen till the pressure of the mixture is 15″ of mercury above the atmospheric pressure.

TABLE II

*Oxidation of cellulose with a mixture of nitrogen dioxide and oxygen at atmospheric pressure*

| Time of reaction hours | Carboxyl content (Neale's method) in milliequivalents per 100 g. material | Copper number | |
|---|---|---|---|
| | | Before treatment with alkali | After treatment with alkali |
| 8 | 49·91 | 71·68 | |
| 16 | 66·82 | 76·76 | 29·08 |
| 24 | 71·91 | 77·09 | |
| 32 | 79·25 | 78·45 | 28·53 |
| 40 | 96·99 | 74·39 | |
| 48 | 99·63 | 84·52 | 25·69 |

tion (1% or 2%) and become more or less completely soluble after the —COOH content has reached 8% or more. Maximum solubility appears to have been attained after five minutes contact with alkali and longer periods upto about 24 hours seem to have no appreciable effect. Shrinkage is first observed when the —COOH content is about 5% and then increases progressively with an increase in —COOH content, reaching a maximum shrinkage of about 75% of the original length when the carboxyl content is about 9%. The oxycellulose samples which are soluble in dilute caustic soda solutions are also soluble in dilute solutions of sodium carbonate, quaternary ammonium hydroxides and in warm aqueous pyridine. Though they retain their fibrous structure

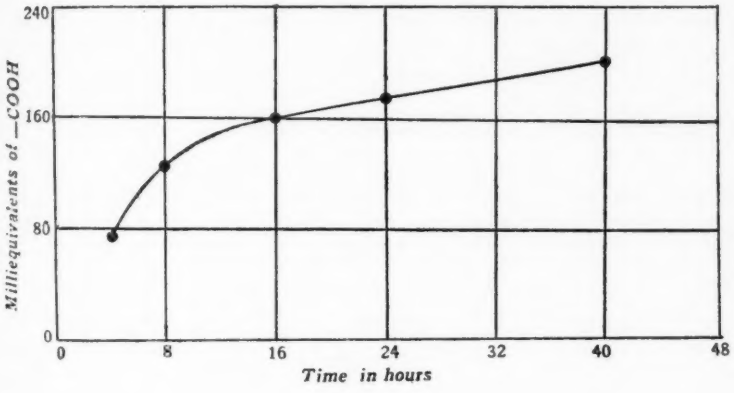



FIG. 1

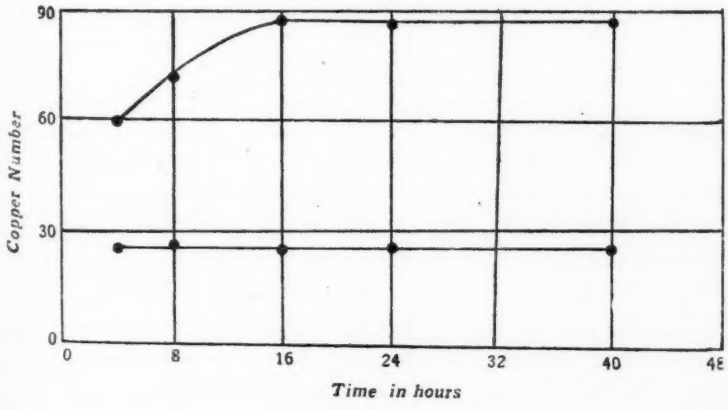



FIG. 2

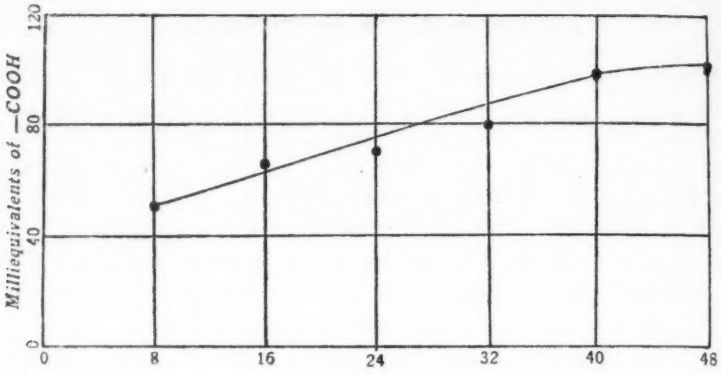



FIG. 3

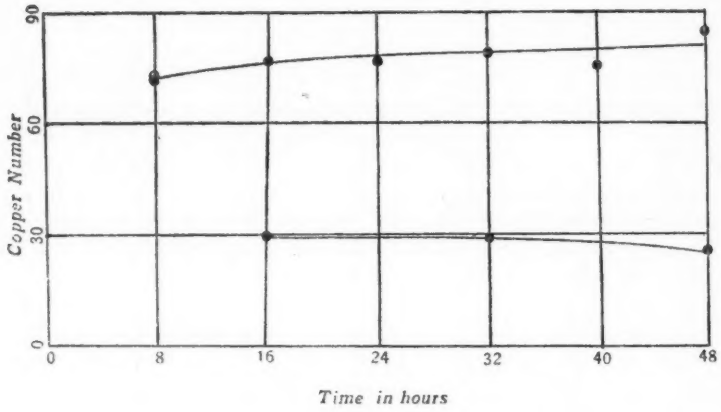



FIG. 4

**Materials : 20 g. bone-dry cotton in 10 l. flask. Oxidant : 10 ml. of nitrogen dioxide (measured at 0° C.) + oxygen till the pressure of the mixture is atmospheric.**

even with a high degree of oxidation, their fluidities in cuprammonium hydroxide are very high. Thus a 2% solution of an oxycellulose possessing a —COOH content of 9% is 76 reciprocal poises, while the fluidity of the solvent at the same temperature (30° C.) is 99·2 reciprocal poises.

In Table II are summarised the properties of oxycelluloses obtained using a mixture of nitrogen dioxide and oxygen at atmospheric pressure. The relation between the time of oxidation and carboxyl content and copper number are represented graphically in Figs. 3 and 4 respectively. It is evident

that though the carboxyl content by Neale's method increases progressively with the time of oxidation, the copper number is more or less constant and is reduced to about ⅓ on treatment with alkali. No shrinkage is observed even after 48 hours and the oxycelluloses obtained are not at all soluble in dilute alkali. However, these products exhibit behaviour similar to the products obtained with the oxidant under pressure, with reference to (*a*) rise in copper number with time of reaction and (*b*) fall in copper number on treatment with alkali (compare Tables I and II and Figs. 2 and 4).

From Tables I and II it is seen that the amount of nitrogen dioxide in the gaseous mixture is the same, only the percentage of oxygen is different. An examination of the above tables and Figs. 1, 2, 3 and 4 brings out clearly the influence of the proportion of oxygen in the oxidation mixture, *viz.*,

(*a*) The rate of reaction is nearly doubled with a higher proportion of oxygen.

(*b*) The reaction seems to have come more or less to a standstill with the reaction mixture containing a lower proportion of oxygen while with the higher proportion of oxygen the rate of reaction seems to be appreciable even after 48 hours. Further the curve for the rate of reaction in the latter case resembles that obtained by Kenyon[17] for oxidation of cellulose with nitrogen dioxide (*cf.* Fig. 5).

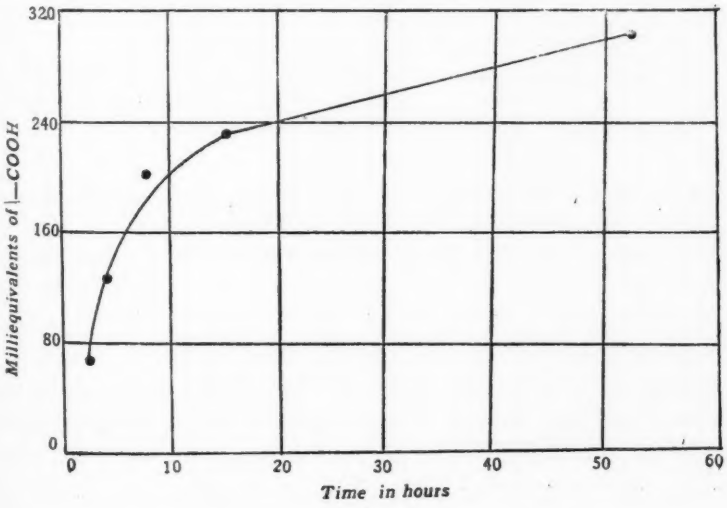



FIG. 5

(*c*) In presence of oxygen, the copper number increases rapidly to a maximum and then remains constant. Alkali treatment results in a fall to approximately one-third of the original.

A comparison of the properties of the nitrogen dioxide + oxygen oxycelluloses (Method A, *cf.* Table I) with nitrogen dioxide oxycelluloses studied by Kenyon and collaborators, is summarised in Table III. Under Kenyon's oxycellulose the original observations of Kenyon, *et al.*, have been summarised.

TABLE III

| Kenyon's nitrogen dioxide oxycellulose | Nitrogen dioxide + oxygen oxycellulose |
|---|---|
| (i) Alkali-soluble only when carboxyl content is 13·5% or more. Samples with lower carboxyl content only swell in dilute alkali | (i) Completely soluble in alkali when carboxyl content is about 9%, but is partly soluble when carboxyl content is above 3·5% |
| (ii) Shrinkage and surface hardening observed when the carboxyl content is more than 15% | (ii) Shrinkage and surface hardening observed with a carboxyl content of 5·5% and above |
| (iii) Oxidation comes more or less to a standstill when the carboxyl content has attained a value of 25% (the theoretical value for poly-anhydro-glucuronic acid) | (iii) Attempts to prepare pure samples with more than 13·5% carboxyl did not succeed due to excessive swelling of the product in water to form a gel during washing treatment |
| (iv) Copper number increases progressively with oxidation. The copper number increases on treatment with alkali. This observation is not recorded by Kenyon and others, but has been observed in the present investigation (*cf.* Table V) | (iv) Copper number rises rapidly, reaches a maximum value at an early stage of oxidation and then remains constant. On treatment with alkali copper number falls to one-third of the original |
| (v) Highly oxidised products are hydrolysed by boiling water and the aqueous extract darkens on further boiling | (v) Highly oxidised samples are only partly hydrolysed by boiling water. The aqueous extract does not darken on boiling |

SIMILARITIES

(1) Both products are highly acidic, possess great affinity for basic dyes and metal ions, and retain their fibrous structure even though highly oxidised.

(2) In aqueous solution sodium salts are precipitated on addition of a water-miscible non-solvent, *e.g.*, ethyl alcohol.

(3) Polyvalent cations form insoluable salts.

From the foregoing, it is evident that nitrogen dioxide + oxygen oxycelluloses (hereafter designated as Oxycellulose I) possess distinctly different properties from the nitrogen dioxide oxycelluloses of Kenyon (hereafter designated as Oxycellulose II.)

*Comparison of the chemical properties of oxycellulose I, oxycellulose II, periodic acid oxycellulose and dichromate-oxalic acid oxycellulose.*—Due to

the excessive handling necessary for the preparation and complete analysis of the oxycellulose samples it was felt that a considerable portion will be lost thus rendering the final sample far from truly representative of the original oxycellulose. Further, it has already been shown that from the point of view of chemical behaviour there is no difference between the two oxycelluloses described in Tables I and II respectively. Therefore moderately oxidised samples of oxycellulose I have been prepared by Method B. Side by side samples of oxycellulose II and two specific oxycelluloses, *viz.*, periodic acid and dichromate-oxalic acid oxycelluloses of a moderate degree of modification have been prepared for comparison. They have been examined with respect to carboxyl content (Neale's method[12] and Iodimetric method[8]) copper number, effect of alkali treatment on copper number and nitrogen content before and after treatment with chlorous acid (Table V).

Due to the high reducing power exhibited by some of the samples, a few samples have been treated with chlorous acid for 18, 42 and 66 hours respectively. The solution of chlorous acid is replaced by a fresh lot of the solution after the first eighteen hours. From the results summarised in Table IV it is evident that treatment with chlorous acid for eighteen hours is sufficient. Hence all the samples described in Table V have been treated with chlorous acid for eighteen hours only.

TABLE IV

*Effect of time of treatment with chlorous acid*

| Properties | Oxycellulose I No. 1 | Time of treatment with chlorous acid in hours | | | Oxycellulose II No. 7 | Time of treatment with chlorous acid in hours | | |
|---|---|---|---|---|---|---|---|---|
| | | 18 | 42 | 66 | | 18 | 42 | 66 |
| Carboxyl content in milliequivalents per 100 g. of the material— | | | | | | | | |
| Alkalimetry .. | 58·5 | 65·4 | 65·0 | 65·4 | 82·4 | 88·1 | 88·4 | 88·1 |
| Iodimetry .. | 57·2 | 63·5 | 63·5 | 63·5 | 84·3 | 90·6 | 89·6 | 90·1 |
| Copper number .. | 37·7 | 34·6 | | 34·6 | 17·0 | 15·3 | | 15·3 |
| Combined nitrogen % | 0·72 | 0·72 | | 0·72 | 0·13 | 0·13 | | 0·13 |

TABLE V

*Comparison of the chemical properties of nitrogen dioxide + oxygen, nitrogen dioxide, periodic acid and dichromate – oxalic acid oxycelluloses*

| Sample No. | Type of oxycellulose and method of preparation | Carboxyl content in milli-equivalents per 100 g. of material | | | | Copper number | | | | Increase in carboxyl content (4) – (2) = (9) | Fall in copper number before alkali treatment (5)–(7)=(10) | Copper number equivalent (9) : (10)=(11) | Colour of alkaline extract during pre-treatment with alkali during the determination of (6) and (8) | | Combined nitrogen content % | Fall in copper number due to alkali treatment | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Before treatment with chlorous acid | | After treatment with chlorous acid | | Before treatment with chlorous acid | | After treatment with chlorous acid | | | | | | | | | |
| | | Neale's (1) | Iodimetry (2) | Neale's (3) | Iodimetry (4) | Before alkali treatment (5) | After alkali treatment (6) | Before alkali treatment (7) | After alkali treatment (8) | (9) | | | Before treatment with chlorous acid | After treatment with chlorous acid | | Before treatment with chlorous acid | After treatment with chlorous acid |
| | *Oxycellulose I* Method B (3 ml. $NO_2$+10 g. cotton) | | | | | | | | | | | | | | | | |
| 1 | Time of reaction 2 hrs. | 58·5 | 57·2 | 65·4 | 63·5 | 37·7 | 15·45 | 34·6 | 15·6 | 6·3 | 3·1 | 2·06 | D. Y. | Y. | 0·72 | −22·2 | −19·0 |
| 2 | ,, ,, 4 hrs. (4 ml. $NO_2$+10 g. cotton) | 72·5 | 72·8 | 76·5 | 78·0 | 40·6 | 19·1 | 38·0 | 18·1 | 5·2 | 2·6 | 2·0 | D. Y. | Y. | 0·90 | −21·5 | −19·9 |
| 3 | Time of reaction 2 hrs. | 22·6 | 20·6 | 33·48 | 29·30 | 14·2 | 9·18 | 10·2 | 7·94 | 8·7 | 4·0 | 2·18 | D. Y. | Y, | 0·40 | − 5·02 | − 2·26 |
| 4 | ,, ,, 4 hrs. | 63·0 | 59·1 | 67·9 | 69·0 | 37·1 | 16·3 | 32·3 | 14·6 | 9·9 | 4·8 | 2·06 | D. Y. | Y. | 0·80 | −20·8 | −17·7 |
| | *Oxycellulose II* (up to 10) (Gaseous $NO_2$ oxidant) | | | | | | | | | | | | | | | | |
| 5 | 3·5 ml. $NO_2$ for 10 g. cotton in 3 l. flask 2 hrs. | 11·1 | 10·1 | 13·1 | 13·2 | 6·02 | 6·5 | 2·58 | 3·1 | 3·1 | 3·44 | 0·90 | L. Y. | P. C. | 0·14 | + 0·48 | + 0·52 |
| 6 | ,, ,, 4 hrs. | 33·1 | 31·6 | 35·1 | 36·2 | 9·75 | 10·2 | 4·73 | 5·1 | 4·6 | 5·02 | 0·92 | L. Y. | P. C. | 0·16 | + 0·45 | + 0·37 |
| 7 | 3·5 ml. $NO_2$ for 10 g. cotton in 1 l. flask 2 hrs. | 82·4 | 84·3 | 88·2 | 90·1 | 17·0 | .. | 11·7 | .. | 5·8 | 5·3 | 1·09 | L. Y. | P. C. | 0·13 | − .. | − .. |
| 8 | ,, ,, 4 hrs. | 119·9 | 121·4 | 119·9 | 124·3 | 20·1 | 21·2 | 17·12 | 19·3 | 2·9 | 3·0 | 0·97 | L. Y. | P. C. | 0·16 | + 1·1 | + 2·18 |
| | (Oxidant: Nitrogen dioxide dissolved in $CCl_4$) | | | | | | | | | | | | | | | | |
| 9 | 10 g. dry cotton treated with 4 ml. $NO_2$ (0° C.) in 175 ml. of dry $CCl_4$ for 4 hours | .. | 32·39 | 36·14 | 36·81 | 6·43 | 6·93 | 3·01 | 3·77 | 3·42 | 3·42 | 1·00 | L. Y. | P. C. | 0·16 | + 0·50 | + 0·76 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 10 | 30 g. dry cotton treated with 5·1 ml. $NO_2$ (0°C.) in 500 ml. dry $CCl_4$ for 4 hours | 16·1 | 16·8 | 20·3 | 20·5 | 8·74 | 11·64 | 4·49 | 5·65 | 3·7 | 4·25 | 0·87 | L.Y. | P. C. | 0·0 | + 2·9 | + 1·16 |
| 11 | Product 10 oxidised with 0·01 M $HIO_4$ for 48 hours at room temperature | 49·6 | 16·8 | 69·6 | 72·0 | 26·8 | 19·4 | 5·46 | 6·88 | 55·2 | 21·34 | 2·59 | Y. | P. C. | 0·0 | − 7·4 | + 1·42 |
| | *Oxycellulose III* | | | | | | | | | | | | | | | | |
| 12 | 21·2 g. (air-dry) cotton treated with 0·01M $HIO_4$ for 48 hours | 30·1 | 2·29 | 47·6 | 46·8 | 19·0 | 12·3 | 1·53 | 1·53 | 44·5 | 17·47 | 2·54 | Y. | P. C. | .. | − 6·7 | + 0·0 |
| 13 | 21·2 g. (air-dry) cotton treated with 0·005 M $HIO_4$ for 48 hours | 12·7 | 2·66 | 25·2 | 25·3 | 10·2 | 8·1 | 1·02 | 1·05 | 22·6 | 9·18 | 2·46 | Y. | P. C. | .. | − 2·1 | + 0·03 |
| | *Oxycellulose IV* | | | | | | | | | | | | | | | | |
| 14 | 21·2 g. (air dry) cotton treated with 0·4N $K_2Cr_2O_7$ in N oxalic acid for 4 hours | 8·58 | 7·87 | 24·4 | 25·6 | 20·2 | 21·3 | 2·54 | 3·2 | 17·73 | 17·66 | 1·00 | Y. | P. C. | .. | + 1·1 | + 0·66 |
| 15 | 21·2 g. (air-dry) cotton treated with 0·2N $K_2Cr_2O_7$ in N oxalic acid for 4 hours | 5·50 | 4·92 | 16·0 | 15·3 | 11·73 | 12·5 | 1·53 | 2·55 | 10·38 | 10·2 | 1·02 | Y. | P. C. | .. | + 0·77 | + 1·02 |

*D. Y.* = Deep Yellow ; *Y.* = Yellow ; *L. Y.* = Light Yellow ; *P. C.* = Practically colourless.

In the above table only the mean of two independent determinations are given for the sake of convenience of expression.

Maximum variation from mean value ± 0·2 units for carboxyl content.

,, ,, ,, ,, ± 0·1 unit for copper number.

A few samples have been examined for cuprammonium fluidity before and after treatment with chlorous acid. The results are summarised in Table VI.

TABLE VI

*Effect of treatment with chlorous acid on cuprammonium fluidity*

| Material | Cuprammonium Fluidity 1% solution | | | | Decrease in cuprammonium fluidity % |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | Mean | |
| *Oxycellulose I* | | | | | |
| No. 1 .. | 52·6 | 50·9 | 49·8 | 51·1 | 38·4 |
| Above treated with chlorous acid .. | 31·8 | .. | 31·2 | 31·5 | |
| No. 2 .. | 50·7 | 51·1 | 49·4 | 50·4 | 32·4 |
| Above treated with chlorous acid .. | 33·7 | .. | 34·5 | 34·1 | |
| *Oxycellulose II* | | | | | |
| No. 5 .. | 28·9 | .. | 29·0 | 28·95 | 17·7 |
| Above treated with chlorous acid .. | 23·9 | 23·7 | 23·8 | 23·8 | |
| No. 6 .. | 41·5 | 40·8 | 41·1 | 41·1 | 15·3 |
| Above treated with chlorous acid .. | 34·2 | 34·5 | 35·7 | 34·8 | |
| *Oxycellulose III* | | | | | |
| No. 12 .. | 53·0 | 51·5 | 53·1 | 52·5 | 43·1 |
| Above treated with chlorous acid .. | 29·6 | 29·9 | .. | 29·8 | |
| *Oxycellulose IV* | | | | | |
| No. 14 .. | 31·6 | .. | 31·0 | 31·3 | 18·0 |
| Above treated with chlorous acid .. | 25·4 | 26·0 | 25·6 | 25·7 | |

The similarities and dissimilarities between the four oxycelluloses are summarised below:

1. For the same degree of oxidation, as measured by carboxyl content, I possesses a higher copper number as compared with II.

2. I possesses a higher percentage of combined nitrogen than II.

3. On treatment with chlorous acid the carboxyl content as determined by the Iodimetric method increases and copper number decreases in both the cases. But if the value of the "copper number equivalent" (*cf.* Table V) is examined it is found that for II and IV the value is nearly unity, for III and

nitrogen dioxide periodic acid oxycellulose No. 11, (which has a preponderance of dialdehyde groups) the value is near about 2·5, while for oxycellulose I it is between 2 and 2·2 which is much nearer to 2·5 than to unity. Another noteworthy point is the small amount of free aldehyde present, (as shown by treatment with chlorous acid) in comparison with the carboxyl groups in the oxycelluloses.

4. I suffers a fall in copper number on treatment with alkali, both before and after treatment with chlorous acid, while II and IV show an increase in copper number under similar treatment. On the other hand however, III suffers a fall in copper number prior to treatment with chlorous acid, but alkali treatment has practically no effect on copper number, if the sample has been pretreated with chlorous acid. The anomalous behaviour of oxycellulose No. 11 is interesting in that, prior to treatment with chlorous acid, alkali treatment results in a fall in copper number, while pretreatment with chlorous acid reverses the effect of alkali treatment.

5. All the oxycelluloses suffer a fall in cuprammonium fluidity on treatment with chlorous acid. A careful examination of Table VI reveals that the percentage decrease is of the same order for oxycelluloses I and III, and II and IV respectively.

6. Further, it may be observed that during tretment with alkali in the course of the study of the effect of alkali treatment on copper number, oxycelluloses II, III, IV and No. 11 give yellow coloured extracts with alkali, if they have not been pretreated with chlorous acid. On pretreatment with chlorous acid however, the alkaline extracts obtained are practically colourless. With oxycellulose I, however, pretreatment with chlorous acid results in a decrease in the colour intensity of the alkaline extract, still the colour of the alkaline extract is quite appreciable.

*Mechanism of oxidation.*—In the foregoing pages the difference between oxycelluloses I and II have been clearly brought out. Kenyon, *et al.*, have shown that when cellulose is oxidised by nitrogen dioxide the primary alcoholic group is oxidised to carboxyl.[1, 2] After an investigation[3] into the oxidation of cellulose by solutions of nitrogen dioxide in carbon tetrachloride they have suggested a mechanism of oxidation. According to these authors, the oxidation of cellulose involves at least two steps, the first of which is nitration. They maintain that it is virtually impossible to prepare an anhydrous cellulose, as powerful desiccants ultimately begin to remove the "water of constitution" from cellulose. Hence they conclude that some nitric acid will be present in any scheme for oxidising cellulose with nitrogen dioxide. The nitration is more or less limited to the primary hydroxyl group in presence

of nitrogen dioxide. The second step is denitration-carboxylation by nitrogen dioxide which is catalysed by the nitric acid present. Thus the mechanism of oxidation of cellulose by nitrogen dioxide may be represented by the following:

$$2N_2O_4 + H_2O \rightarrow 2HNO_3 + N_2O_3 \quad (1)$$

$$(C_5H_7O_4\cdot CH_2OH)_x + XHNO_3 \rightarrowtail (C_5H_7O_4\cdot CH_2O\cdot NO_2)_x + XH_2O \quad (2)$$

$$(C_5H_7O_4\cdot CH_2ONO_2)_x \xrightarrow[HNO_3]{XN_2O_4} (C_5H_7O_4\cdot COOH)_x + \frac{3X}{2} N_2O_3 \quad (3)$$

Now it is evident from the above equations that the concentration of nitrogen dioxide decreases progressively with time. However, if oxygen is present the dinitrogen trioxide ($N_2O_3$) formed is immediately reoxidised to nitrogen dioxide. Thus the effective concentration of nitrogen dioxide will be maintained more or less constant as long as any oxygen is present. In this manner a much higher rate of oxidation of the cellulose by nitrogen dioxide may be expected in presence of excess of oxygen. Another interesting possibility is the side by side oxidation of cotton cellulose during the reoxidation of dinitrogen trioxide to nitrogen dioxide. Auto-oxidations of this type are well known both in organic and inorganic chemistry.[18-24]

In the foregoing pages it has been shown that when cellulose is oxidised with a mixture of nitrogen dioxide and oxygen, the products obtained differ from Kenyon's oxycelluloses. Thus it is evident that in addition to the oxidation of the primary alcoholic group in 6-position to carboxyl, some other position is also being oxidised in the cellulose molecule when a mixture of nitrogen dioxide and oxygen is used as the oxidant. From the earlier analysis of the experimental results it can be concluded that nitrogen dioxide + oxygen oxycelluloses possess the following groups:

(*a*) Carboxyl groups as indicated by the Iodimetric method.

(*b*) Free aldehyde groups as shown by increase in carboxyl content and decrease in copper number on treatment with chlorous acid.

(*c*) A substantial proportion of the aldehyde groups are of the type that are present in periodic acid oxycelluloses, as seen from the "copper number equivalent" of 2 to 2·2 shown by these oxycelluloses as compared with 2·5 the corresponding value for periodic acid oxycelluloses (*cf.* Table V). This is further borne out by the degree of decrease in cuprammonium fluidity exhibited by these oxycelluloses on treatment with chlorous acid (*cf.* Table VI).

(*d*) A group which exhibits reducing properties on treatment with alkaline Braidy solution, but not affected by chlorous acid, but which is substantially destroyed by treatment with strong alkali. This is probably

the nitrate group present in these oxycelluloses and which accounts for the combined nitrogen. A glance at Table V will show that these oxycelluloses possess a higher percentage of combined nitrogen than nitrogen dioxide oxycelluloses.

In attempting to explain the mechanism of decomposition of nitric acid esters by alkalis Berthelot[25] suggested that it may take place in the following way:

$$R{\cdot}CH_2O{\cdot}NO_2 + OH' \rightarrow R{\cdot}CHO + NO_2' + H_2O \qquad (4)$$

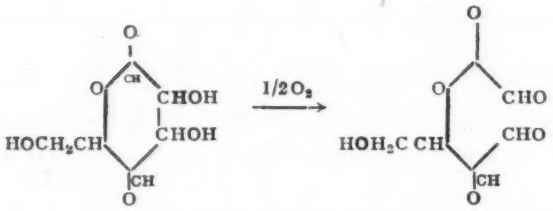
Further Kenyon and Grey[26] have shown that cellulose nitrates decompose intramolecularly with the reduction of nitrate nitrogen to nitrite, and oxidation of the cellulose molecule to simple organic acids. It is also well known that during the saponification of cellulose nitrate with alkali, the decomposition products formed exert a reducing effect on the sodium nitrate, so that the latter is partially converted into nitrite and partly into nitrogen and ammonia.[27–29]

If it is assumed that equation (4) represents the reaction that takes place in presence of the weak alkali of the Braidy solution, then the high copper number of these oxycelluloses can be explained. Further, if in presence of the stronger alkali employed in the pre-treatment, it is assumed that the reactions suggested by Kenyon and Gray,[26] and other workers,[27–29] take place, then the substantial fall in copper number exhibited by these oxycelluloses on treatment with strong alkali can also be accounted for. This is further substantiated by the fact that the oxycellulose No. 11, which contains the dialdehyde type of grouping, suffers a fall in copper number on alkali treatment. But if the same oxycellulose is first treated with chlorous acid, alkali treatment has exactly the opposite effect on copper number, as the dialdehyde groups have been rendered insensitive by treatment with chlorous acid.

Thus it appears that during the oxidation of cellulose with a mixture of nitrogen dioxide and oxygen a certain amount of nitration takes place. Also at the same time the ring structure appears to be ruptured at the 2 : 3 position with the formation of a dialdehyde as in the periodic acid oxidation of cellulose in addition to the carboxyl. The exact position of the carboxyl group is very difficult to fix as it may be formed in the 6-position as suggested by Kenyon's mechanism or by partial oxidation of the dialdehyde with nitrogen dioxide to the corresponding dicarboxylic acid. The small proportion of the free aldehyde in comparison with the carboxyl content in these oxycelluloses as also in nitrogen dioxide oxycelluloses can be explained if it is assumed that the first stage in the oxidation is the

formation of the aldehyde either in the 6-position or the dialdehyde in the 2 : 3 position, thus:

$$R{\cdot}CH_2OH \xrightarrow{1/2\,O_2} R{\cdot}CHO + H_2O \qquad (5)$$




(6)

The second stage will be the oxidation of these aldehyde groups to carboxyl groups by the nitrogen dioxide present. Now if the oxidation of —CHO→COOH is much more rapid than the formation of —CHO as described above then the small amount of free aldehyde can be easily accounted for.

## Summary

(*i*) When cellulose is oxidised with a mixture of nitrogen dioxide and oxygen the products obtained (I) dissolve in dilute alkali when the carboxyl content is about 9% as compared with a minimum of 13·5% required for alkali solubility in case of nitrogen dioxide oxycelluloses (II).

(*ii*) I usually possesses a higher percentage of combined nitrogen than II.

(*iii*) The yellow colour developed on treatment with hot dilute caustic soda disappears more or less completely if the oxycelluloses (except I) are treated with chlorous acid. In case of I, the intensity of the colour is diminished considerably.

(*iv*) There is a greater decrease in cuprammonium fluidity on treatment with chlorous acid with I and periodic acid oxycelluloses as compared with II and dichromate oxalic acid oxycelluloses.

(*v*) On treatment with alkali there is a fall in copper number both in the case of I and periodic acid oxycellulose while an increase in copper number takes place in the case of II and dichromate-oxalic acid oxycellulose. Based on the above conclusions a tentative mechanism of oxidation has been suggested for the oxidation of cellulose with a mixture of nitrogen dioxide and oxygen.

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# STUDIES IN OXYCELLULOSE

## Part IV. Chemical Behaviour of Accelerated Oxidation Oxycelluloses

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### Introduction

It is now generally recognized that when cellulose is oxidized in presence of another easily oxidizable substance, an accelerated oxidation takes place.[1-6] This accelerated oxidation is comparable to the widely occurring auto-oxidations well known both in inorganic and organic chemistry.[7-12]

During their investigation of the accelerated oxidation of cellulose with sodium hypochlorite solution in presence of leuco vat dyes, Turner, Nabar and Scholefield[3] observed a close similarity between the pH-fluidity relationship and the pH-oxidation potential relationship and hence concluded that the mechanism of oxidation must be relatively simple and consistent over the whole pH range. Later, choosing Cibanone Orange R in the leuco form as the best example of the activation of the hypochlorite, unaccompanied by interference from any part of the dye molecule, the above authors[4] have found that the hypochlorite oxidation of cellulose accelerated by a reduced vat dye takes a different course and gives rise to products distinctly different from those obtained with prolonged oxidation. The important contribution of Nabar, Scholefield and Turner to the study of the mechanism of accelerated oxidation of cellulose is the constant ratio obtained between the reducing and the acidic groups formed in the products of accelerated oxidation as distinct from that obtained by the slow normal oxidation of cellulose.[4] The conditions of oxidation such as pH of the oxidising medium, its strength and the time of treatment did not affect this ratio.

With a view to elucidate the mode of oxidation and examine the possibility of explaining the relationship between the various chemical properties of the oxycelluloses, the present investigation has been undertaken.

Leuco Cibanone Orange R dyed cotton has been oxidized using buffered sodium hypochlorite solution and carefully washed and dried. The various

chemical properties of the oxycelluloses have been examined before and after treatment with chlorous acid.

Investigation into the mechanism of accelerated oxidation of cotton cellulose by hypochlorite in presence of leuco compounds of vat dyes which are affected by hypochlorite[14] is in progress.

*General Details of Experimental Methods*

*Materials.*—The cotton used for the experiments was 2/28's gassed supercombed fully bleached yarn. After thorough washing in hot and in cold water, the cotton had the following properties: (*a*) Copper number (Micro-Braidy method)[15] = 0·015. (*b*) Cuprammonium fluidity (B.C.I.R.A. method 0·5% solution)[16] = 4·6. (*c*) Carboxyl content (Neale's method)[17] per 100 g. of cellulose = 1·0 m.e.

The cotton is dyed with Cibanone Orange R by the method described in the previous communication[18] taking 2% of the solid commercial dye on weight of the cotton. The dyeing and reoxidation, washing, drying and conditioning of the dyed yarn is carried out in a dark room. The dyed yarn had a slightly higher copper number, cuprammonium fluidity and carboxylic acid content than the undyed cotton.

*Reduction of the dyeing and its hypochlorite treatment.*—The reduction of the dyeing is carried out using 2% cold sodium hydrosulphite solution followed by washing in air-free distilled water to remove the hydrosulphite. The reduced washed dyeing is then treated for ten minutes with buffered sodium hypochlorite solution as described in the previous communication.[18]

*Oxidation of the Cibanone Orange R oxycellulose with chlorus acid.*—10 Grams of the air-dry sample is oxidized by treatment with 0·1M sodium chlorite in 0·5M phosphoric acid for 18 hours at room temperature. The product thus obtained is washed thoroughly, rendered cation free, dried and stored as before.

*Determination of copper number.*—The copper number has been determined by Heyes' micro method[15] modified as described in the earlier communication.[14]

*Determination of carboxyl content.*—(*a*) *Neale's method*[17].—One gram of the cation-free dry material is suspended in a mixture of 25 ml. of 0·02N caustic soda (carbonate-free), 25 ml. of 5% sodium chloride and 25 ml. of carbon dioxide-free distilled water. At the end of one hour the excess of alkali is back titrated with 0·02N hydrochloric acid using Bromo-cresol-Purple as indicator.

(*b*) *Iodimetric method.*[19]—This method has been described in detail in a previous communication. In this method one gram of cation-free dry material is suspended in a mixture of 25 ml. of KI-$KIO_3$-NaCl solution (83 g., 21·4 g., and 50 g. respectively/litre), 25 ml. of 0·02N sodium thiosulphate and 25 ml. of carbon dioxide-free distilled water. At the end of twenty-four hours the excess of thiosulphate is back titrated with 0·02N iodine solution using starch as indicator.

*Experimental Results and Discussion*

Leuco-Cibanone Orange R impregnated cotton has been oxidized using buffered hypochlorite solutions. About half of the oxycellulose sample thus produced has been treated with chlorous acid as described earlier. The various chemical properties of the oxycelluloses thus produced have been examined and the results are summarized in Table I.

TABLE I

*Effect of hypochlorite treatment followed by subsequent treatment with chlorous acid on Leuco-Cibanon Orange R impregnated cotton cellulose*

| Sample No. | Treatment given | Carboxyl content in m.e. per 100 g. of sample (Mean value from two determinations) | | Copper No. (Mean value from two determinations) | Corrected for original value of "O" and "OA" as the case may be | | |
|---|---|---|---|---|---|---|---|
| | | | | | Carboxyl content corrected | | Copper No. corrected |
| | | Neale's | Iodimetry | | Neale's | Iodimetry | |
| 1 | Treated with hypochlorite pH 5·5 | 2·84 | 2·51 | 2·96 | 1·63 | 1·21 | 2·89 |
| 1A | "1" treated with chlorous acid | 4·48 | 4·13 | 1·42 | 3·09 | 2·73 | 1·36 |
| 2 | Treated with hypochlorite pH 7·1 | 3·94 | 3·17 | 4·58 | 2·73 | 1·87 | 4·51 |
| 2A | "2" treated with chlorous acid | 6·22 | 5·43 | 2·24 | 4·83 | 4·03 | 2·18 |
| 3 | Treated with hypochlorite pH 9·05 | 2·72 | 2·39 | 2·85 | 1·51 | 1·09 | 2·78 |
| 3A | "3" treated with chlorous acid | 4·23 | 4·08 | 1·35 | 2·84 | 2·62 | 1·29 |
| 0 | Untreated dyeing | 1·21 | 1·30 | 0·07 | .. | .. | .. |
| 0A | "0" treated with chlorous acid | 1·39 | 1·40 | 0·06 | .. | .. | .. |

From this table it is seen that copper numbe rdecreases and the carboxyl content increases on treatment of accelerated oxidation oxycelluloses with chlorous acid. Further, it is noteworthy that even after all the free aldehydic

groups have been oxidized to carboxyl by treatment with chlorous acid, the values for carboxyl content of the treated oxycelluloses as determined by the Iodimetric method[19] are lower than those obtained by Neale's alkali titration method.[17]

It has now been established that accelerated oxidation oxycllulcses show a constant ratio,[4,14,20] between the copper number and carboxyl content as determined by Neale's method.[17] This is interesting since it has been shown by Davidson[21] that Neale's method gives fictitious values for reducing oxycelluloses. Further, it is interesting to note that when the carboxyl content is determined by the Iodimetric method[19] which is independent of the presence of free aldehyde groups, even then a constant ratio is obtained between copper number and carboxyl content as is clearly indicated in Table II (columns J and K). This constant ratio with both the methods is very striking and lends sufficient support to the validity of the results obtained by previous workers[3,4,20] in spite of the strong criticism against Neale's method[17] of carboxyl determination by Davidson,[21] and others.[22]

If the constant ratio in the above two cases is to be accepted as an indication of a definite mechanism of degradation independent of the pH of the oxidizing medium then the results outlined in Table I have to be analysed on the following basis:

(1) Relation between carboxyl content by Alkalimetry and Iodimetry.

(2) Effect of treatment with chlorous acid on copper number.

(3) Effect of treatment with chlorous acid on carboxyl content.

(4) Relation between decrease in copper number on treatment with chlorous acid and residual copper number.

(1) *Relation between carboxyl content by Alkalimetry and Iodimetry.*— As has already been pointed out, the values for carboxyl content for Cibanone Orange R accelerated oxidation oxycelluloses as determined by Iodimetric method are lower than those obtained by Neale's alkali, titration method even after the oxycelluloses have been treated with chlorous acid. It can be seen from columns G and H of Table II that the difference between the carboxyl content as determined by Alkalimetry and Iodimetry is practically unaffected by treatment with chlorous acid. This indicates that there is some alkali-labile group present which is not affected by treatment with chlorous acid.

TABLE II

*Relation between the various chemical properties of the accelerated oxidation oxycelluloses*

| Sample No. | (Carboxyl content corrected) Before chlorous acid treatment | | After chlorous acid treatment | | Copper number (corrected) Before chlorous acid treatment | After chlorous acid treatment | Difference in values of carboxyl content as determined by the two methods | | Copper No. −COOH before chlorous acid treatment | | Initial Copper No. Residual Copper No. | Final carboxyl Initial carboxyl | | Free aldehyde expressed as fall in copper number E−F=P | Free aldehyde/alkali labile group (expressed as residual copper number) P/F =Q |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C | D | E | F | A−B=G | C−D=H | E/A=J | E/B=K | E/F=L | C/A=M | D/B=N | | |
| 1 | 1·63 | 1·21 | 3·09 | 2·73 | 2·89 | 1·36 | 0·42 | 0·36 | 1·77 | 2·38 | 2·12 | 1·89 | 2·26 | 1·53 | 1·13 |
| 2 | 2·73 | 1·87 | 4·83 | 4·03 | 4·51 | 2·18 | 0·86 | 0·80 | 1·66 | 2·42 | 2·08 | 1·77 | 2·16 | 2·33 | 1·07 |
| 3 | 1·51 | 1·09 | 2·84 | 2·62 | 2·78 | 1·29 | 0·42 | 0·22 | 1·84 | 2·55 | 2·16 | 1·88 | 2·41 | 1·49 | 1·16 |

*N. B.*—The corrected values for carboxyl content and copper number in columns *A* to *F* in the above table have been taken from the last three columns of Table I.

This is further borne out by the results shown in Table III.

TABLE III

*Effect of prolonged action of alkali on accelerated oxidation oxycelluloses*

| Sample No. | Material | COOH content in milliequivalents per 100 g. | | | | | Copper number |
|---|---|---|---|---|---|---|---|
| | | Time of contact in hours. | | | | | |
| | | 1 | 32 | 48 | 96 | 144 | |
| 2 | Cibanone Orange R oxycellulose | 3·95 | 8·46 | .. | 14·05 | 16·36 | 4·58 |
| 2A | Above treated with chlorous acid | 6·16 | 8·46 | .. | 11·85 | 13·65 | 2·24 |
| 4 | Dichromate oxalic acid oxycellulose | 8·58 | 20·2 | 24·9 | 33·78 | 33·04 | 20·2 |
| 4A | Above treated with chlorous acid | 24·4 | 24·4 | 26·36 | .. | 25·64 | 2·54 |
| 5 | Periodic acid oxycellulose | 12·7 | .. | 25·16 | 29·50 | 34·35 | 10·2 |
| 5A | Above treated with chlorous acid | 25·20 | .. | 26·10 | 26·60 | 27·58 | 1·02 |

*N.B.*—The corrected values for carboxyl content and copper number in columns *A* to *F* in the above table have been taken from the last three columns of Table I.

In this table is shown the effect of treatment with chlorous acid on the alkali lability of the oxycelluloses. While all the three oxycelluloses, *viz.*, the Cibanone Orange R accelerated oxidation oxycellulose, the periodic acid oxycellulose and the dichromate oxalic acid oxycellulose exhibit alkali lability before treatment with chlorous acid, only the Cibanone Orange R accelerated oxidation oxycellulose shows a much higher alkali lability after treatment with chlorous acid than the other two.

(2) *Effect of chlorous acid treatment on copper number.*—It is extremely interesting to find (*cf.* columns E, F and L, Table II) that in the case of Cibanone Orange R accelerated oxidation oxycellulose, the residual copper number after treatment with chlorous acid forms a substantial portion of the original copper number. On the contrary the residual copper number is only a small percentage of the original copper number with the periodic acid and dichromate-oxalic acid oxycelluloses (*cf.* Tables I and III). It may be said that the alkali-labile group referred to above which affects the determination of carboxyl content by Alkalimetry on standing, also exhibits reducing property under alkaline conditions, while in acidic medium is not free to get oxidized by chlorous acid.

(3) *Effect of chlorous acid treatment on carboxyl content.*—It is evident from columns M and N (Table II) that the carboxyl content before treat-

ment with chlorous acid bears a definite ratio with the carboxyl content after treatment with chlorous acid.

(4) *Relation between fall in copper number on treatment with chlorous acid and residual copper number.*—Since only free aldehydic groups are oxidized by chlorous acid to carboxyl,[23,24] it may be safely assumed that the decrease in copper number on treatment with chlorous acid may be taken as a measure of the free aldehyde groups present in the oxycellulose.

That the ratio $\frac{\text{fall in copper number}}{\text{residual copper number}}$ is more or less the same for the oxycelluloses examined is clearly shown in Table II Column Q.

From the foregoing analysis of the results it is clear that Cibanone Orange R accelerated oxidation oxycelluloses possess the following chemical properties:

(*i*) Free carboxylic acid groups as shown by the Iodimetric method.

(*ii*) Free aldehyde groups as shown by, (*a*) the copper number and (*b*) an increase in carboxyl content and a reduction in copper number on treatment with chlorous acid.

(*iii*) An alkali-labile reducing group which is unaffected by acidic oxidation with chlorous acid, but which is available for oxidation in the alkaline Braidy solution, and also which influences the determination of carboxyl content by Alkalimetry.

(*iv*) The free reducing groups and the alkali-labile reducing groups are present in a constant ratio.

When these properties are taken together, it becomes quite evident how complicated it is to assign a structural formula, to the oxycelluloses described above, which will explain all these properties.

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# ANTHRAQUINONE AND ANTHRONE SERIES

## Part VI. 6- and 8-Benzamidopyrimidanthrones

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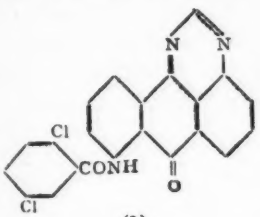
AMONG the commercial vat dyes whose constitution was unknown at the commencement of the present programme of work on anthraquinone vat dyes, two were Indanthrene Yellow 4GK and Indanthrene Yellow 7GK. Both the dyes were introduced were recently by the IG Farbenindustrie as vat dyes giving bright yellow and lemon-yellow shades, which do not accelerate the photochemical oxidation of cellulose. It is well known that this catalytic activity is a serious defect of many yellow and orange anthraquinonoid vat dyes.

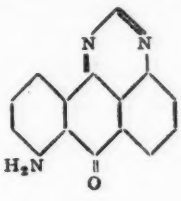
Commercial Indanthrene Yellow 4GK is a fine yellow powder which dyes cotton yellow shades from a wine-red alkaline hydrosulphite vat. After purification from its diluents by boiling with 5% hydrochloric acid, it crystallized from nitrobenzene in yellow needles melting at 287–88°. The dye contained nitrogen and chlorine, and on hydrolysis by 20% alcoholic potassium hydroxide at the boil or by 90% sulphuric acid on the water-bath, it broke down into a base and an acid, the latter being identified as 2:5-dichlorobenzoic acid. During alkaline hydrolysis the colour of the substance changed from yellow to brown-red, while by acid hydrolysis the progress of the reaction was indicated by the rapid change of the colour of the solution from orange to olive. At the end of the hydrolysis the alcoholic caustic potash mixture was diluted with a large amount of water to precipitate the base completely. The red-brown base which separated was collected and dissolved in hot concentrated hydrochloric acid. On basifying the acid solution, a red-violet precipitate was obtained. The alkaline filtrate gave on acidification a precipitate of 2:5-dichlorobenzoic acid.

The base, which crystallized from nitrobenzene in red-violet needles, m.p. 256–57°, was diazotizable and on heating the diazonium salt with alcohol and copper sulphate, the deaminated product was obtained as pale brown-yellow needles from acetic acid, m.p. 242–43°. The substance contained nitrogen, and dissolved in concentrated hydrochloric acid, indicat-

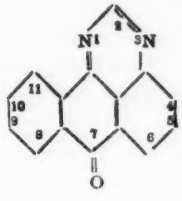
ing its basic character, due apparently to nitrogen present in a ring system. The analysis and properties showed that it was probably 1 : 9-pyrimidanthrone (III). The IG have described 8-aminopyrimidanthrone (II) as a brown-red substance melting at 257° and the 2 : 5-dibenzoyl derivative of




(I)




(II)



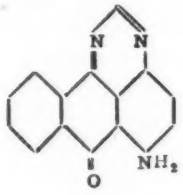

(III)

the amine as a yellow dye, m.p. 287°. The constitution of Indanthrene Yellow 4GK is therefore 8-(2′ : 5′-dichloro-)benzamidopyrimidanthrone (I).

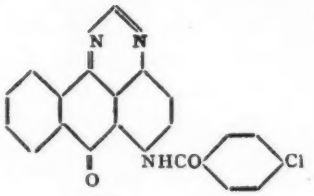
8-Aminopyrimidanthrone (II) was synthesized[2] by heating 1 : 5-diaminoanthraquinone under reflux with excess of formamide in dry phenol in presence of anhydrous ammonium chloride and cuprous chloride. 8-Aminopyrimidanthrone remained in solution in hot phenol and was recovered on steam distillation. The red-brown substance insoluble in phenol did not melt up to 360°, gave a green solution in concentrated sulphuric acid, and was probably 1 : 9 : 5 : 10-anthradipyrimidine.[3] 8-Aminopyrimidanthrone crystallized from nitrobenzene in red-violet needles, m.p. 257°, undepressed when mixed with the base obtained from Indanthrene Yellow 4GK. It gave an olive solution in concentrated sulphuric acid, from which a garnet precipitate was obtained on dilution. The 2 : 5-dichlorobenzoyl derivative of 8-aminopyrimidanthrone was yellow and crystallized from nitrobenzene in yellow needles, m.p. 287–88°, which was undepressed when mixed with the pure dye isolated from Indanthrene Yellow 4GK. It gave an orange solution in concentrated sulphuric acid and a wine-red alkaline hydrosulphite vat.

Indanthrene Yellow 7GK is a fine yellow powder, dyeing cotton lemon-yellow from a brown-red alkaline hydrosulphite vat. Diluents were removed by means of 5% hydrochloric acid, and on crystallization from nitrobenzene, it was obtained as yellow needles melting at 317°. It was hydrolysed by heating with 90% sulphuric acid for a few hours into a base and an acid. The acid component was found to be *p*-chlorobenzoic acid. The base was obtained from nitrobenzene as yellow-brown needles, m.p. 277–78°. This base was much less soluble in concentrated hydrochloric acid than the amine obtained by the hydrolysis of Indanthrene Yellow 4GK,

but like the latter it was diazotizable. Removal of the amino group, *via* the diazonium salt, gave a substance crystallizing in yellow needles, m.p. 242–43°, undepressed when admixed with 1 : 9-pyrimidanthrone (III) obtained from Indanthrene Yellow 4GK. The IG have described[4] 6-aminopyrimidanthrone (IV) as a yellow compound, m.p. 277°, and its *p*-chlorobenzoyl derivative as a yellow dye, m.p. 317°, giving lemon-yellow shades.[1] The constitution of Indanthrene Yellow 7GK is therefore 6-(*p*-chloro-)benzamidopyrimidanthrone (V). Since this work was completed (1946), the




(IV)



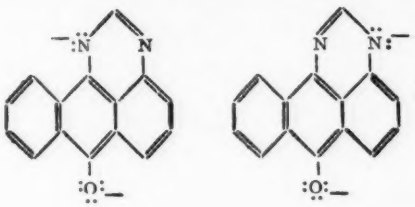

(V)

constitution of Indanthrene Yellow 4GK and 7GK has been published in one of the reports on the German dyestuff industry.[4]

6-Aminopyrimidanthrone (IV) was prepared by heating 1 : 4-diaminoanthraquinone with 30% formaldehyde and 30% ammonia in presence of *m*-nitrobenzenesulphonic acid at 90–95° for 15 hours.[4] The amine crystallized from nitrobenzene in greenish-yellow needles, m.p. 277–78°, undepressed by mixing with the base obtained from Indanthrene Yellow 7GK. Its *p*-chlorobenzoyl derivative crystallized in lemon-yellow needles, m.p. 317°, undepressed when mixed with Indanthrene Yellow 7GK.

The only reference to pyrimidanthrones and the vat dyes derived from it are in the patent literature. The preparation of pyrimidanthrone from α-aminoanthraquinone by heating it with formamide was first described in 1909,[5] but the value of the acylamidopyrimidanthrones as vat dyes seems to have been realized much later, since the dyes were marketed in 1934 or 1935, and the relevant patents appeared in 1932–34. As vat dyes, the pyrimidanthrones are unique in their possession of a single carbonyl group. All anthraquinone vat dyes can be divided into two distinct types: derivatives of anthraquinone and derivatives of anthrone. The ability of the first type to function as vat dyes is due to the anthraquinone nucleus, which is reduced under alkaline conditions to anthrahydroquinone, soluble in alkali; when suitable groups are present to impart the necessary substantivity or affinity for cellulose, the dye becomes applicable by the usual vat-dyeing process. An anthrone derivative, such as benzanthrone or an amino or benzamidobenzanthrone, does not have vat-dyeing properties

unless the molecule is doubled by appropriate methods of condensation, so that the compound contains a pair of carbonyl groups connected by a conjugate chain and thus forms a quinonoid system. The vatting properties of pyrimidanthrone result from an increase in the acid strength of the leuco



(III A) (III B)

compound (a dihydropyrimidanthrone) by the resonance stabilization of the negative ion as indicated in structures (III A) and (III B). Pyrimidanthrone therefore forms an alkali-soluble leuco compound on reduction, and when a benzamido group is present in the molecule, the affinity of the leuco compound for cellulose becomes adequate for dyeing purposes.[6]

Strong absorption in the region 3600–4000 A has been considered to be concerned in the photochemical activity of yellow and orange vat dyes, and it has been shown that the safe dye Indanthrene Brilliant Orange GR has negligible absorption at 3600–4000 A.[7] However, 1-benzamidoanthraquinone (Algol Yellow WG), an active dye, as well as Indanthrene Yellow 4GK and Indanthrene Yellow 7GK have similar absorption curves (Fig. 1); the pyrimidanthrones have considerably higher intensity of absorption in the region 4200–4500 A.

From a study of the available data and the relevant theoretical considerations, the activity of a dye in accelerating the photochemical oxidation of cellulose would appear to depend on a combination of several factors of which the colour is only one. Shaffer[8] has drawn attention to the rapidity of oxidations and reductions involving one-electron changes, in contrast to the slow ionic reactions involving simultaneous two-electron changes such as ($Tl^{++} \rightarrow Tl^{+++}$) or ($I_2 \rightarrow 2I^-$). He regards the catalytic activity of quinones as being due to their ability to accept electons singly, and he has indicated the relation of this property of reversible organic oxidation-reduction systems to the reduction of oxygen to hydrogen peroxide in biological oxidations. Semiquinone formation is probably also significant in the photochemical degradation of cellulose in presence of anthraquinone derivatives, moisture and alkali having a marked effect on the action. Michaelis and Smythe have postulated as a general principle that " the inertia of organic compounds

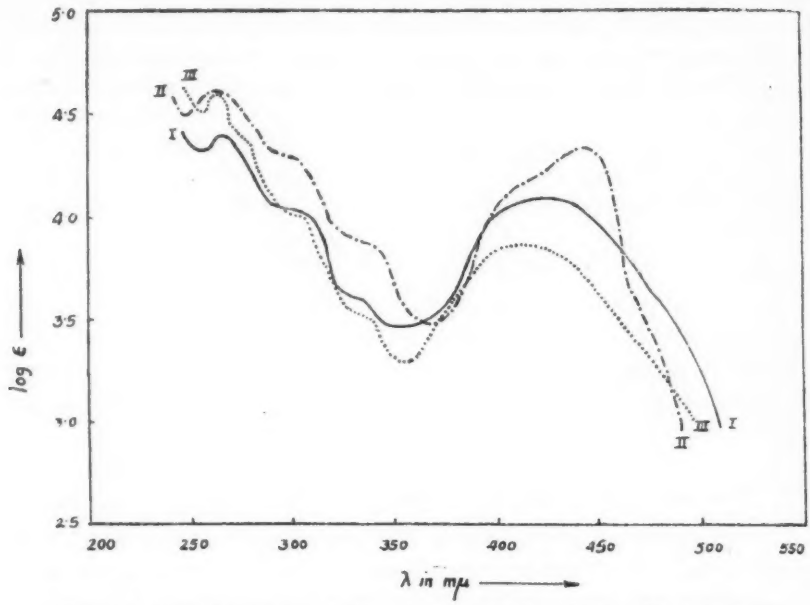
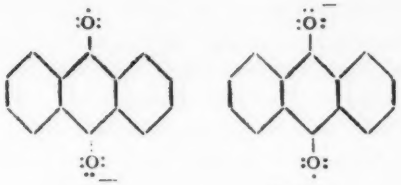



FIG. 1. Absorption spectra of (I) Indanthrene Yellow 4 GK, (II) Indanthrene Yellow 7GK, and (III) α-Benzamidoanthraquinone (in cellosolve).

towards oxidizing agents is due to the fact that the oxidation can proceed at a measurable speed only in two successive univalent steps and consequently only if the intermediate free radical can be formed."[9] Thus oxidations are rapid if there is resonance-stabilization of the semiquinone radicals. Appleton and Geake have obtained from the redox titrations of vat dye systems evidence of the formation of the intermediate semiquinones in several instances.[10] Visual evidence was especially striking in the case of Indanthrene Golden Yellow GK (2:3:7:8-dibenzopyrene-1:6-quinone), which gives a clear red vat of the dihydro compound and a blue semiquinone. We suggest that the redox potential of the quinone, which is known to be a measure of its oxidizing power, and the stability of the anionic semiquinone are both concerned in the acceleration of the photochemical oxidation of cellulose by certain anthraquinonoid vat dyes, together with their light absorption characteristics which determine the quanta of energy available.

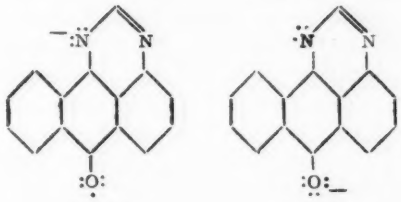
The semiquinone anion from anthraquinone is stable because of the equivalence of the two structures (VI A) and (VI B). Yellow dyes such as Indanthrene Yellow FFRK and Anthraflavone are very active, and four



(VI A) (VI B)

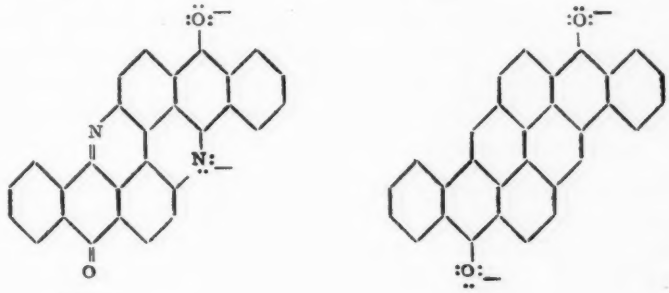
equivalent structures can be written for the semiquinone ion of the dihydro compound.

The stability of the semiquinone ion of a pyrimidanthrone must be relatively small, since the structures (VII A) and (VII B) are not equivalent, and the pyrimidanthrone derivatives, Indanthrene Yellow 4GK and 7GK, are therefore comparatively inert in catalysing the photochemical oxidation of cellulose. The difference between flavanthrone and pyranthrone, the latter being much more active as a tenderer, may be attributed to a similar reason. The anions of the normal leuco compounds (or dihydro derivatives)



(VII A) (VII B)

of flavanthrone and pyranthrone are constituted as (VIII) and (IX) respectively,[10] so that an oxygen atom and a nitrogen atom in flavanthrone, in contrast to two oxygen atoms in pyranthrone, are involved in the reduction process. Thus the semiquinone ion of pyranthrone will be stabilized



(VIII) (IX)

by resonance between equivalent structures in which the odd electron is on one or other of the two oxygen atoms, while the two structures contributing to the resonance of the semiquinone ion of flavanthrone are not equivalent, since in one the odd electron will be on an oxygen atom and in the other on a nitrogen atom. Although qualitative evidence of semiquinone formation during the oxidation of the normal leuco compound has been obtained in both cases,[10] it is very probable that the semiquinone ion of pyranthrone has considerably greater stability.

## Experimental

*Indanthrene Yellow 4GK (I). Purification of Commercial Indanthrene Yellow 4GK (I).*—The dye (10 g.) was added slowly with stirring to 5% hydrochloric acid (200 c.c.) and boiled for 30 minutes, stirring occasionally. The mixture was filtered hot, and the lemon-yellow residue (6 g.) was crystallized from nitrobenzene. The yellow needles melted at 287–88° (Found: N, 9·9; Cl, 16·6. $C_{22}H_{11}O_2N_3Cl_2$ requires N, 10·0; Cl, 16·9%).

*Hydrolysis of the dye*: (*a*) *alkaline hydrolysis.*—The dye (3 g.) was refluxed with 20% alcoholic caustic potash (60 c.c.) for 12 hours. The mixture was diluted with water (400 c.c.) and boiled for a few minutes to remove the bulk of the alcohol. Filtered while hot, the red-violet precipitate was collected, and washed free from alkali with hot water. The product (1·8 g.) crystallized from nitrobenzene in red-violet needles, m.p. 256–57°, undepressed when admixed with 8-aminopyrimidanthrone (II) (Found: N, 16·8. $C_{15}H_9ON_3$ requires N, 17·0%). The alkaline filtrate was acidified with dilute hydrochloric acid (10%). The brown precipitate (0·9 g.) on repeated crystallization from water (Norit) gave lustrous colourless needles, m.p. 154°, identified as 2:5-dichlorobenzoic acid. (*b*) *Acid hydrolysis.*—The dye (5 g.) was dissolved in 90% sulphuric acid (50 c.c.). The acid solution was heated on the water-bath for 4 hours, cooled and added to crushed ice. The red-violet precipitate was collected and extracted with sodium bicarbonate solution (10%; 100 c.c.). On acidifying the bicarbonate extract, 2:5-dichlorobenzoic acid (1·4 g.), crystallizing from water (Norit) in colourless needles, m.p. 154°, was obtained. The base (2·7 g.) crystallized from nitrobenzene in brown-red needles, m.p. 257–58°, identical with the product obtained by alkaline hydrolysis.

*Deamination of 8-aminopyrimidanthrone.*—The base (1 g.) was boiled with glacial acetic acid (10 c.c.) and after cooling to 5°, was added with stirring to an ice-cold solution of sodium nitrite (1 g.) in concentrated sulphuric acid (12 g.). The mixture was kept at 5° for 20 minutes. It was then added to boiling alcohol (40 c.c.) containing copper sulphate (0·2 g.)

and the alcoholic mixture was refluxed on the water-bath. On dilution with water (300 c.c.), the pale yellow precipitate was collected. The product (0·9 g.) crystallized from acetic acid in yellow-brown needles, m.p. 242-43° (Found: N, 11·9. $C_{15}H_8ON_2$ requires N, 12·1%). The substance gives a brown-red alkaline hydrosulphite vat; and forms a yellow-brown solution in concentrated sulphuric acid, which turns pale yellow on dilution, and on basifying a pale yellow-brown precipitate separates.

8-*Aminopyrimidanthrone* (*II*).—1 : 5-Diaminoanthraquinone (3 g.), formamide (6 c.c.), anhydrous ammonium chloride (3 g.), anhydrous cuprous chloride (0·5 g.) and dry phenol (30 c.c.) were raised to the boil during one hour, and the reaction mixture, mechanically agitated, was refluxed for 5 hours. It was filtered hot; the brown-red residue (2·5 g.) did not melt up to 340°, and gave a greenish-olive solution in concentrated sulphuric acid. It gave no test for a free amino group. The phenolic filtrate was steam-distilled, and the garnet coloured residue (1·3 g.) was collected. It crystallized from nitrobenzene in dark brown-red needles, m.p. 257–58°, undepressed when admixed with the base obtained from Indanthrene Yellow 4GK (*D.R.P.* 566,474 quotes the same m.p. for 8-aminopyrimidanthrone). It gives a wine-red alkaline hydrosulphite vat, and an olive solution in concentrated sulphuric acid, from which a garnet coloured precipitate is obtained on dilution.

8-(2′ : 5′-*Dichloro-*)*benzamidopyrimidanthrone* (*I*).—2 : 5-Dichlorobenzoic acid (0·5 g.; 1·3 mol.) was refluexed with thionyl chloride (5 c.c.) for two hours. The excess of thionyl chloride was removed by vacuum distillation, and to the acid chloride were added 8-aminopyrimidanthrone (0·5 g.; 1 mol.), and nitrobenzene (10 c.c.). The mixture was refluxed for 2 hours. On cooling a yellow-brown product (0·7 g.) separated. It was purified by dissolving in concentrated sulphuric acid (10 c.c.) and precipitating. The yellow precipitate was stirred in water (35 c.c.), to which sodium bichromate solution (10 c.c.; 10%) was added, and the slurry stirred for three hours at 90°. The deep yellow precipitate was collected (0·65 g.), and it crystallized from nitrobenzene in yellow needles, m.p. 287–88°, undepressed when admixed with purified Indanthrene Yellow 4GK (Found: N, 10·1, $C_{22}H_{11}O_2N_3Cl_2$ requires N, 10·0%).

*Indanthrene Yellow 7GK* (*V*): *Purification.*—The commercial dye (10 g.) was purified, as in the previous case, by treating with 5% hydrochloric acid (200 c.c.). The purified dye (5 g.) crystallized from nitrobenzene in lemon-yellow needles, m.p. 317–18° (Found: N, 11·2; Cl, 9·0%). The substance dissolves in concentrated sulphuric acid with an orange-red colour, and

dyes cotton lemon-yellow shades from a brown-red alkaline hydrosulphite vat.

*Hydrolysis of Indanthrene Yellow 7GK.*—The pure dye (3 g.) was dissolved in concentrated sulphuric acid (60 c.c.). To the acid solution, water (12 c.c.) was added and the solution was heated on the water-bath for 6 hours. It was then cooled and poured into crushed ice, the brown-yellow precipitate was collected and extracted with 10% sodium bicarbonate solution. On acidifying the bicarbonate solution, a colourless precipitate (0·9 g.) separated. It crystallized from alcohol in glistening colourless needles, m.p. 234°, and was identified as *p*-chlorobenzoic acid. The brown-yellow base (1·5 g.) crystallized from nitrobenzene in brown-yellow needles, m.p. 277–78°, undepressed when admixed with 6-aminopyrimidanthrone (IV) (Found: N, 17·0. $C_{15}H_9ON_3$ requires N, 17·0%). The substance dissolves in concentrated sulphuric acid with a crimson-red colour and is sparingly soluble in alkaline hydrosulphite solution.

*Deamination of 6-aminopyrimidanthrone.*—The base (V) (1 g.) was diazotized by the glacial acetic acid and sulphuric acid method, and added to boiling alcohol (40 c.c.), containing copper sulphate (0·2 g.). The mixture was refluxed for two hours; diluted with water (300 c.c.), the yellow precipitate was collected, boiled with concentrated hydrochloric acid, and filtered hot. On basifying the acid solution, a yellow precipitate separated (0·3 g.). It crystallized from acetic acid in fine pale yellow needles, m.p. 242-43°, undepressed when admixed with 1:9-pyrimidanthrone (III) obtained from Indanthrene Yellow 4GK.

6-*Aminopyrimidanthrone (IV)*[4].—Sublimed 1:4-diaminoanthraquinone (3 g.), 30% ammonia (6 g.), 30% formaldehyde solution (6 g.) and Ludigol (2·25 g.) were heated in a sealed tube at 95-100° for 15 hours. The olive-brown crystalline product (3·5 g.) was collected; 1·1 g. of the crude product was dissolved in 96% sulphuric acid (30 g.) and by adding water (15 g.), the sulphate of the amine precipitated. It was filtered through a Gooch crucible, and washed with 58% sulphuric acid. It was treated with hot water and made alkaline with ammonia. The pure product (0·7 g.) crystallized from nitrobenzene in greenish yellow needles, m.p. 277–78°, undepressed when admixed with the amine obtained from Indanthrene Yellow 7GK.

6-(*p'-Chloro-*) *benzamidopyrimidanthrone.*—6-Amino-pyrimidanthrone (0·3 g.; 1 mol.), *p*-chlorobenzoyl chloride (0·25 g.; 1·25 mol.) and nitrobenzene (5 c.c.) were refluxed for 3 hours. The greenish yellow needles were collected and stirred in cold pyridine (10 c.c.) for six hours to dissolve

the unconverted amine. The purified product (0·2 g.) crystallized from nitrobenzene in needles, m.p. 317°, undepressed when admixed with purified Indanthrene Yellow 7GK (Found: N, 10·4. $C_{22}H_{12}O_2N_3Cl$ requires N, 10·9%).

## Summary

Hydrolysis of Indanthrene Yellow 4GK gives 8-aminopyrimidanthrone (II) and 2:5-dichlorobenzoic acid; the dye is therefore the 8-(2′:5′-dichloro)-benzamidopyrimidanthrone (I). Indanthrene Yellow 7GK is the *p*-chlorobenzoyl derivative (V) of 6-aminopyrimidanthrone (IV). The ability of a pyrimidanthrone derivative to function as a vat dye, although it possesses only one carbonyl group, results from an increase in the acid strength of the leuco compound by the resonance stabilization of the anion as indicated in structures (III A) and (III B).

Unlike many yellow and orange anthraquinonoid vat dyes, Indanthrene Yellow 4GK and 7GK do not accelerate the photochemical oxidation of cellulose. Differences in the behaviour of anthraquinone derivatives and of pyrimidanthrone derivatives in the action of light on cellulose are explained on the basis of the relative stability of their semiquinone ions.

## Acknowledgment

We wish to thank the Council of Scientific and Industrial Research for a Fellowship awarded to one of us, and to thank Mr. T. S. Gore for the microanalyses recorded in the paper.

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# NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

## Part XXXI. Synthesis of 3-Hydroxy Primetin and Its Nuclear Oxidation

By T. R. Seshadri, F.A.Sc., S. Varadarajan and V. Venkateswarlu

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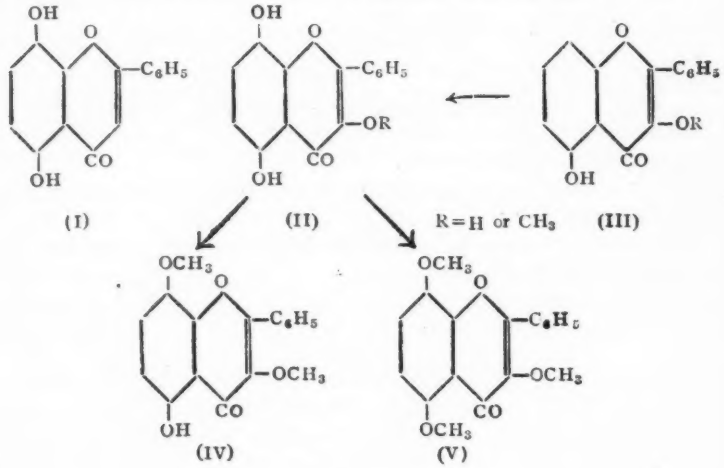
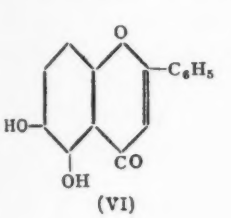
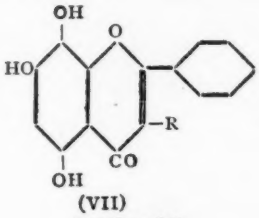
Primetin (I) is one of the special compounds of the flavone group discovered in the plant genus Primula. Though the occurrence of the flavonol analogue, 3-hydroxy primetin (II, R = H) has not yet been recorded, it could also be expected to occur in nature. It has now been synthetically prepared from 3:5-dihydroxy flavone (III, R = H)[1] by a method similar to the one adopted earlier in the synthesis of primetin.[2] The first stage is partial methylation yielding 3-methoxy-5-hydroxy flavone (III, R = $CH_3$), the more resistant 5-hydroxyl being left out. Oxidation of this product with alkaline persulphate produces the quinol (II, R = $CH_3$) having all the expected properties. Partial methylation of (II, R = $CH_3$) using one mole of dimethyl sulphate yields 3:8-dimethoxy-5-hydroxy flavone (IV) and complete methylation using excess of the reagent gives rise to 3:5:8-trimethoxy flavone (V). By demethylation of the quinol (II, R = $CH_3$) with hydriodic acid, 3-hydroxy primetin (II, R = H) is obtained. These compounds are quite distinct from the isomeric 3:5:6-trihydroxy flavone and its derivatives.[3, 4]



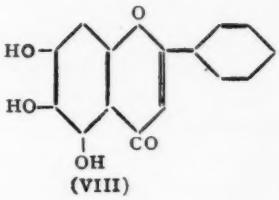
That there was no isomeric change during the above demethylation of (II, R = $CH_3$) and that the product had the expected constitution (3:5:8-trihydroxy flavone) (II, R = H) was evident from its properties. It was further confirmed by its remethylation to yield 3:8-dimethoxy-5-hydroxy flavone (IV). This is an important observation since the ethers of primetin (I) yield only 5:6-dihydroxy flavone (VI) by demethylation with hydriodic acid.[5] Earlier it was noted that derivatives of flavones with the 5:7:8-arrangement of hydroxyl groups (VII, R = H) underwent isomeric change into 5:6:7-hydroxy flavones (VIII) by this treatment (for a consolidated account, see Sastri and Seshadri[6]) but the corresponding flavonol derivatives (gossypetin group) (VII, R = OH) did not,[7] indicating thereby that the presence of a 3-hydroxyl group in the molecule prevents this rearrangement. Primetin (I) and 3-hydroxy primetin (II, R = H) are the simplest representatives of the flavone and flavonol series respectively having the minimum requirements for this study. Their behaviour confirms the importance of the 3-hydroxyl in preventing this isomeric change.



(VI)



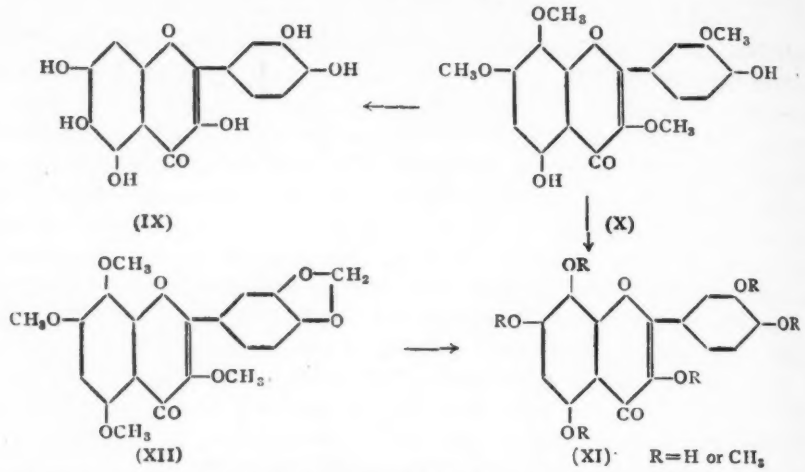
(VII)
R=H or OH



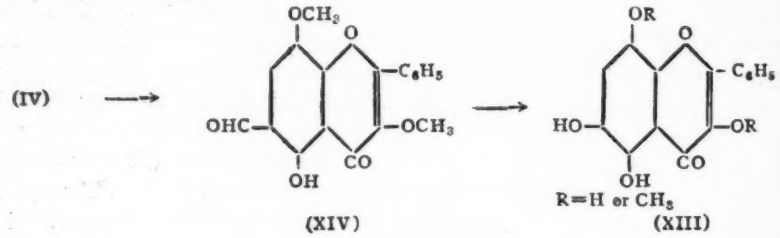
(VIII)

In view of these experimental observations and conclusions, the discussion of Briggs and Locker[8] regarding the constitution of meliternatin and ternatin seems to require careful reconsideration. They claim to have obtained quercetagetin (IX) by the dealkylation of the two compounds. On the analogy of the behaviour of the methyl ethers of the flavones, norwogonin (5:7:8-trihydroxy flavone) and isoscutellarein (5:7:8:4′-tetrahydroxy flavone), they consider that meliternatin and ternatin (X) may be gossypetin derivatives. In support of this contention, it is reported that ternatin (X) on methylation yields gossypetin hexamethyl ether (XI, R = $CH_3$). However, meliternin (XII) which is also a gossypetin derivative is found to yield only gossypetin (XI, R = H) under the same conditions of demethylation. Further work may be expected to clarify these discrepancies.

Recently the nuclear ortho-oxidation of primetin was carried out by Rajagopalan, Seshadri and Varadarajan[9] and 6-hydroxy primetin and its derivatives were obtained. A similar series of reactions starting with 3-




methoxy primetin (II, R = $CH_3$) would lead to the synthesis of 3:5:6:8-tetrahydroxy flavone (XIII, R = H) and its derivatives. The flavonol (XIII, R = H) is the lowest member of the gardenin series and was prepared earlier by Balakrishna and Seshadri[4] in two ways. The feasibility of a new method has now been explored by carrying out the essential stages, (1) partial methylation of 3-methoxy primetin to 3:8-dimethoxy-5-hydroxy flavone (IV), (2) preparation of the 6-aldehyde (XIV) and (3) oxidation with hydrogen peroxide to yield 3:8-dimethoxy-5:6-dihydroxy flavone (XIII, R = $CH_3$). The yields are satisfactory.




## Experimental

### 3-*Methoxy-5-hydroxy flavone* (*III*, *R* = $CH_3$)

3:5-Dihydroxy flavone (1·2 g.) was dissolved in dry acetone (150 c.c.) and dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (3 g.) were added and the mixture refluxed on a water-bath for 6 hours. The potassium salts were then filtered off and washed repeatedly with warm

acetone. The solvent was then distilled off from the filtrate and the residue crystallised twice from alcohol when it came out as pale yellow glistening rectangular plates and prisms melting at 115–16°. Yield 1 g. It gave a deep green colour with ferric chloride in alcoholic solution. It was easily soluble in alcohol and ethyl acetate and sparingly soluble in acetone (Found: C, 71·3; H, 4·8; $OCH_3$, 11·9; $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5 and $OCH_3$, 11·6%).

3-*Methoxy*-5: 8-*dihydroxy flavone* (*II*, $R = CH_3$)

To a solution of 5-hydroxy-3-methoxy flavone (1 g.) in aqueous sodium hydroxide (10 c.c. of 3%) and pyridine (40 c.c.), maintained at 15–16°C., was added dropwise a solution of potassium persulphate (1·5 g. in 40 c.c.) during the course of four hours with continuous stirring. The stirring was continued for two hours more after the addition. The orange red solution along with some undissolved yellow sodium salt was left aside for 24 hours at the end of which time most of the salt had dissolved and the solution assumed a deep red colour. It was cooled in ice and acidified to congo red with concentrated hydrochloric acid. The precipitated yellow unchanged flavone (0·2 g.) was filtered off and the filtrate extracted repeatedly with ether to remove completely all the unreacted compound. To the clear deep red aqueous portion sodium sulphite (1·5 g.) and concentrated hydrochloric acid (25 c.c.) were added and the mixture kept in a boiling water-bath for half an hour. The solution was allowed to cool and the yellow crystalline solid that separated was filtered and washed with water. Ether extraction of the filtrate yielded some more of the dihydroxy compound. When crystallised twice from ethyl acetate it came out in the form of bright yellow rectangular plates melting at 210–12°. Yield 0·25 g. It was readily soluble in alcohol, acetone and ethyl acetate but sparingly in light petroleum. With ferric chloride in alcoholic solution it gave a reddish brown colour and dissolved readily in aqueous sodium hydroxide to give a deep red solution (Found: C, 67·2; H, 4·5; $OCH_3$, 11·0; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2 and $OCH_3$, 10·9%).

3: 8-*Dimethoxy-5-hydroxy flavone* (*IV*)

A solution of 3-methoxy-5: 8-dihydroxy flavone (II, $R = CH_3$) (1·2 g.) in dry acetone (150 c.c.) was refluxed for 6 hours with dimethyl sulphate (0·45 c.c.) and anhydrous potassium carbonate (2 g.). The acetone was filtered off and the potassium salts were washed several times with warm acetone. The pale red semi-solid left on distilling off acetone from the filtrate was crystallised twice from alcohol. It was obtained as pale yellow rectangular plates melting at 140–41°. It gave a green colour with alcoholic

ferric chloride (Found: C, 68·1; H, 4·7; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%).

3:5:8-*Trimethoxy flavone* (*V*)

3-Methoxy-5:8-dihydroxy flavone (II, R = $CH_3$) was methylated with excess of dimethyl sulphate and anhydrous potassium carbonate in dry acetone solution. 3:5:8-Trimethoxy flavone crystallised from dilute alcohol as colourless rectangular plates melting at 120–22° (Found: C, 69·3; H, 5·4; $OCH_3$, 30·0; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1 and $OCH_3$, 29·8%).

3:5:8-*Trihydroxy flavone* (3-*Hydroxy primetin*) (*II, R = H*)

3-Methoxy-5:8-dihydroxy flavone (0·45 g.) was dissolved in acetic anhydride (7 c.c.) and to the cooled solution was added cautiously hydriodic acid (10 c.c., d. 1·7). The mixture was heated in an oil-bath at 140° for 30 minutes, cooled and treated with a saturated solution of sodium bisulphite (60 c.c.). The yellow precipitate (0·35 g.) was filtered, washed with water and when dry, crystallised from ethyl acetate. It came out as short yellow needles melting at 196–98°. With ferric chloride in alcoholic solution, it gave a green colour which rapidly turned reddish brown and with aqueous sodium hydroxide a deep red colour. With *p*-benzo-quinone in alcoholic solution it developed a red colour, characteristic of the presence of hydroxyls in the 5:8-positions (Found: C, 66·4; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%).

*Methylation*

3:5:8-Trihydroxy flavone (0·3 g.) was dissolved in acetone (75 c.c.) and refluxed with dimethyl sulphate (0·2 c.c.) and anhydrous potassium carbonate (1 g.) for 6 hours and the product worked up as usual. The residue left after distillation of acetone crystallised from alcohol as pale yellow rectangular plates melting at 140–41° alone or in admixture with a sample of 5-hydroxy-3:8-dimethoxy flavone (IV) described above.

5-*Hydroxy*-3:8-*dimethoxy-flavone*-6-*aldehyde* (*XIV*)

5-Hydroxy-3:8-dimethoxy flavone (IV) (0·5 g.) and hexamine (2 g.) were heated with glacial acetic acid (15 c.c.) on a boiling water-bath for 6 hours. The solution which was orange red at the beginning turned slowly red. To the hot solution was added a boiling mixture of concentrated hydrochloric acid (10 c.c.) and water (15 c.c.). On cooling, bright yellow crystals of the aldehyde separated out. The mixture was diluted to 200 c.c. with water and left overnight. The yellow crystalline solid was filtered and washed with water. Yield 0·34 g. On crystallisation from alcohol containing a

few drops of acetic acid, it separated out as clusters of short yellow needles melting at 183–84°. It gave a green colour with alcoholic ferric chloride (Found: C, 66·1; H, 4·3; $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%). The dinitrophenyl-hydrazone of the aldehyde, prepared in the usual manner, melted at 274–76°.

5:6-*Dihydroxy*-3:8-*dimethoxy flavone* (*XIII*, $R = CH_3$)

The above aldehyde (0·67 g.) was dissolved in pyridine (30 c.c.) and to the yellow solution was added aqueous sodium hydroxide (5·0 c.c., N/2). The colour of the solution changed to red. The solution was cooled to 0° and hydrogen peroxide (4·1 c.c. 5%) was added drop by drop with shaking in the course of ten minutes. The flask was corked and left at room temperature for two hours. The red colour changed slowly to yellow again. The solution was acidified with concentrated hydrochloric acid, the precipitated yellow solid filtered and washed with water. Yield 0·4 g. It crystallised from ethyl acetate as very fine yellow feathery needles melting at 267–68°. It was sparingly soluble in alcohol and acetone. With ferric chloride it gave a green colour and dissolved in dilute alkali to give a yellow solution (Found: C, 64·6; H, 4·5; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%).

## Summary

3-Hydroxy primetin has been synthesised starting with 3:5-dihydroxy flavone and using partial methylation, para nuclear oxidation and final demethylation. During the last stage no isomeric change is noticed. This is in conformity with the behaviour of similar cases of flavonol derivatives and is different from the behaviour of analogous flavone derivatives. Ortho-oxidation of 3-hydroxy primetin leading to the synthesis of the lowest member of the gardenin series is found to proceed satisfactorily.

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# SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

## Part XIII. Constitution of Prunetin and Its Synthesis

By N. Narasimhachari and T. R. Seshadri, F.A.Sc.

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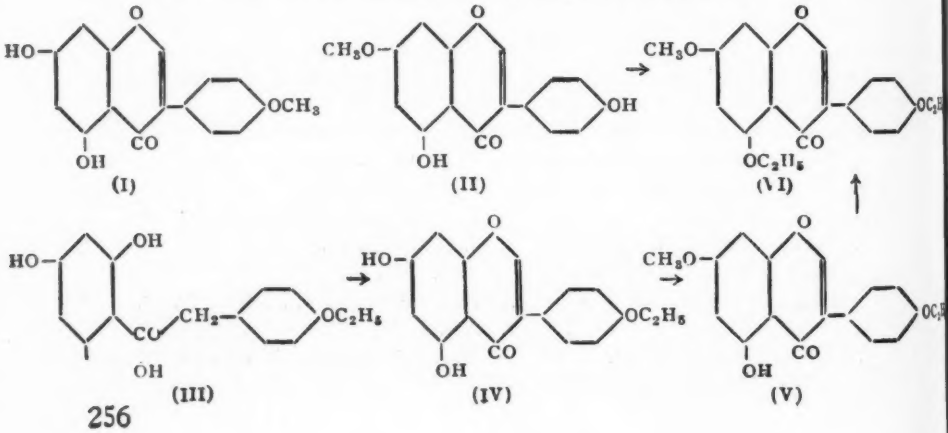
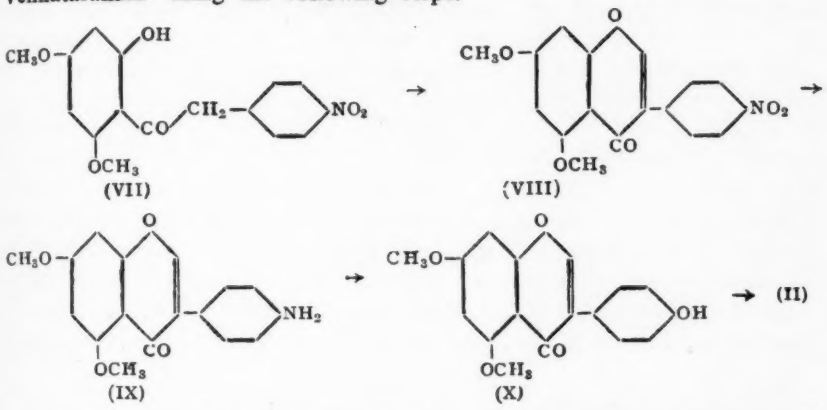
Received June 16, 1950

That prunetin was a monomethyl ether of the isoflavone genistein was established by Baker and Robinson.[1] Since it underwent partial methylation to yield a monomethyl ether,[2] it was clear that the resistant 5-hydroxyl was free in the molecule. Consequently the 7 or 4′ position should carry the methoxyl group. This point was unsettled till Shriner and Hull[3] synthesised the 4′-methyl ether (I) which differed from prunetin, but was found to agree with another naturally occurring monomethyl ether, biochanin-A.[4] By elimination, therefore, prunetin should be the 7-methyl ether of genistein (II). A stricter synthetic proof could be provided by completely ethylating prunetin and establishing the constitution of the diethyl ether by synthesis. This is now reported in this paper. By the condensation of phloroglucinol and *p*-ethoxy-phenyl-acetonitrile and converting the resulting ketone (III) into isoflavone, 4′-O-ethyl genistein (IV) is obtained. This is then partially methylated using one mole of dimethyl sulphate. As in all similar cases the methyl group goes into the 7-position leaving the resistant 5-hydroxyl free; the properties of the product agree with this constitution (V). Final complete ethylation yields 7-methoxy-5:4′-diethoxy isoflavone (VI) which is found to be identical with the diethyl ether of prunetin.

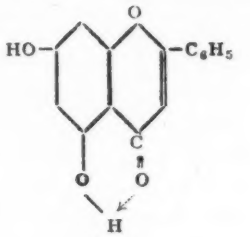


A synthesis of prunetin has recently been announced by Iyer, Shah and Venkataraman[5] using the following steps.




A simpler method which would appear to be significant for the study of biogenesis is described in this paper; it is based on the following considerations. In Part XII[6] of this series it was pointed out that among the monomethyl ethers of anthoxanthins of different types, the most numerous have the methoxyl group in the 7-position. This would suggest that they are probably formed in nature by direct methylation of this position. Two alternatives have then to be considered. Either the hydroxyl in this position is definitely more reactive than those in other positions or there exists a mechanism which protects the other groups from methylation. Very little seems to be known about the second alternative except that the 5-hydroxyl group is chelated and therefore definitely resistant to methylation. Regarding the first alternative the position may be stated as follows. Partial monomethylation of hydroxy flavones has so far been successful only in the case of chrysin (XI)[7], the simplest of dihydroxy flavones; the success in this case is easily understood, since in chrysin the two hydroxyl groups differ considerably in reactivity. Tectochrysin (XII) can be conveniently made in the laboratory by this partial methylation. But when more hydroxyl groups are present particularly in the side phenyl nucleus, the difference between these and the 7-hydroxyl is far less marked and the success of partial monomethylation in the flavone group does not seem to be so definite. Perkin and Horsfall[8] made attempts to prepare a monomethyl ether of luteolin by direct methylation by means of methyl iodide and alkali and recorded that they could get only the 7: 4′-dimethyl ether (XIII) in a small yield. Thus in this case the 4′-hydroxyl is as reactive as the 7-hydroxyl. Examining carefully other related groups of anthoxanthins some of them seemed

to offer greater possibilities. For example, Shinoda and Sato[9] recorded that they could methylate naringenin (XIV) with restricted quantities of diazomethane to yield sakuranetin (XV). Our earlier attempt[10] to repeat this by the more convenient method employing dimethyl sulphate and potassium carbonate in dry acetone solution was not successful because no suitable procedure for the purification of the product and removing unchanged naringenin and its dimethyl ether was available. This has now been worked out using solubility in dilute aqueous sodium carbonate (5%) and aqueous sodium hydroxide (2%). Actually the explanation of this partial methylation and of the successful separation of the mixture involves one and the same principle. Of the three hydroxyls in naringenin (XIV), the one in the 5-position is resistant owing to chelation with the neighbouring carbonyl. There exists appreciable difference between the other two hydroxyl groups also; the one in the 7-position is more acidic because of conjugation

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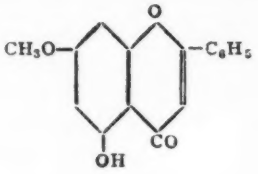


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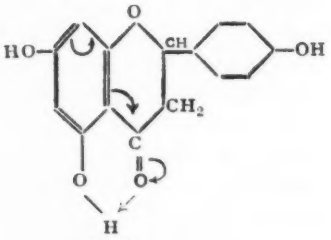


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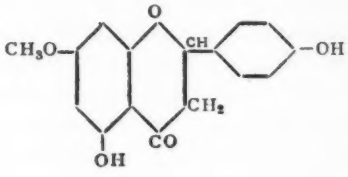


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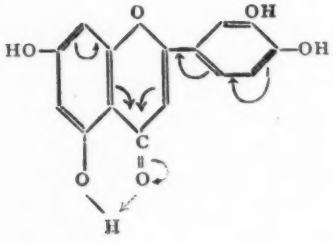
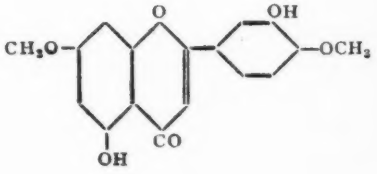


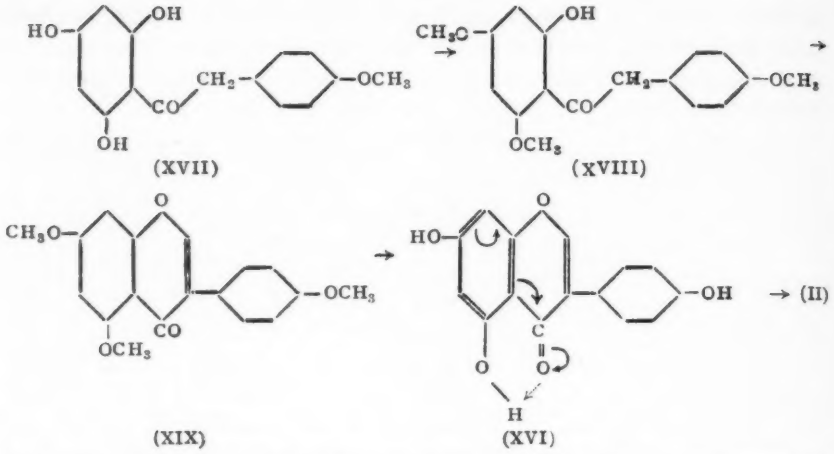

(XIII)

with the carbonyl (vinylogy) whereas the one in the side-phenyl nucleus is not conjugated. As a consequence the 7-hydroxyl is more readily methylated and further its presence renders the compound soluble in aqueous sodium carbonate.

The same considerations become applicable to the isoflavone genistein (XVI) though the structural causes are different. In the flavanones the oxygen ring has no ethylenic double bond conjugating the side-phenyl ring with the carbonyl group whereas in the isoflavones the side-phenyl nucleus is in the α-position with reference to the C = O group and thus conjugation is averted. Consequently a simplified synthesis of prunetin by the partial methylation of genistein should be possible. This has now been achieved and the results are reported in this paper. Earlier Walz[11] seems to have reported the isolation of a monomethyl ether of genistein by direct methylation with methyl iodide. Its melting point was recorded as 189–91° and its structure as 5 : 7-dihydroxy-4′-methoxy isoflavone. But it does not agree with the description of biochanin-A with which it should be identical according to his surmise or of prunetin as could be expected from the considerations discussed above. Detailed study of this product was not recorded by Walz. It was most probably a mixture. In our experiments using dimethyl sulphate no detectable quantity of biochanin-A (4′-methyl-genistein) was met with.

Genistein required for our experiments was obtained by the demethylation of prunetin and also by synthesis in the following manner. Phloroglucinol was condensed with *p*-methoxy-phenyl-acetonitrile and the resulting ketone[1] (XVII) partially methylated using two moles of dimethyl sulphate to yield the 2-hydroxy-4 : 6 : 4′-trimethoxy ketone (XVIII). This trimethoxy ketone was prepared earlier by Robertson, *et al.*[12] from phloroglucinol-dimethyl ether and *p*-methoxy-phenyl acetonitrile. It was finally converted into genistein-trimethyl ether (XIX). The isoflavone condensation proceeds much better in this case than with (XVII) as originally adopted by Shriner and Hull.[3] Final demethylation yielded genistein in good yield.

Partial methylation of genistein (XVI) with one mole of dimethyl sulphate proceeded satisfactorily. From the resulting mixture genistein was removed by macerating with cold aqueous sodium carbonate. The insoluble portion was treated with cold aqueous sodium hydroxide (2%) in which prunetin dissolved leaving out the higher methylation products. It was recovered by acidification and recrystallised. A yield of 20% could be obtained. The synthetic product agreed with natural prunetin from *Prunus puddum*[2] in every respect and yielded identical derivatives. The diethyl




ether was compared with synthetic 5:4′-diethoxy-7-methoxy isoflavone and found to be identical.

## Experimental

2:4:6-*Trihydroxy-phenyl-4′-ethoxy-benzyl ketone* (*III*):

A solution of phloroglucinol (5g.), *p*-ethoxy-phenyl-acetonitrile[13] (5 g.) and zinc chloride (1 g.) in dry ether (100 c.c.) was cooled in ice, saturated with dry hydrogen chloride for 4 hours and left in the ice-chest overnight. Ether was then decanted off and the pale yellow solid ketimine hydrochloride dissolved in water and heated on a boiling water-bath for 1 hour. On cooling, the ketone separated as a colourless crystalline solid. It crystallised from dilute methyl alcohol as colourless prisms melting at 208–10° (Found: in a sample dried at 110° *in vacuo*: C, 62·4; H, 6·1; $C_{16}H_{16}O_5$, $H_2O$ requires C, 62·7; H, 5·9%.)

5:7-*Dihydroxy-4′-ethoxy isoflavone* (IV):

Powdered sodium (1 g.) was cooled in ice and treated with an ice-cold solution of the above ketone (2 g.) in ethyl formate (10 c.c.) with shaking. After keeping in the refrigerator for 48 hours, pieces of ice were added and the excess of ethyl formate was removed under reduced pressure. The residue was extracted with ether and the ether layer separated and washed with aqueous bicarbonate. On evaporating the resulting ether solution a pale yellow solid was left behind. By acidifying the aqueous layer and extracting with ether more of the substance could be obtained; but it was less pure. Total yield 0·5 g. 5:7-Dihydroxy-4′-ethoxy isoflavone crystallised from ethyl acetate-petroleum ether mixture as colourless prisms melting

at 238–40°. It gave a pink colour with ferric chloride and dissolved in aqueous sodium carbonate (Found: C, 64·2; H, 5·3; $C_{17}H_{14}O_5$, $H_2O$ requires C, 64·5; H, 5·1%.)

*Partial methylation to 5-hydroxy-7-methoxy-4′-ethoxy isoflavone (V):*

The above dihydroxy compound (IV) (0·5 g.) was methylated by refluxing with dimethyl sulphate (0·2 c.c.) and anhydrous potassium carbonate (0·5 g.) for 6 hours in acetone solution. It crystallised from alcohol as colourless needles melting at 142–4°. It gave a deep red colour with ferric chloride and was sparingly soluble in aqueous sodium hydroxide (Found: C, 68·8; H, 5·3; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%.)

*Ethylation to 7-methoxy-5:4′-diethoxy isoflavone* (VI):

The 5-hydroxy compound (V) was refluxed in dry acetone solution with excess of ethyl iodide and anhydrous potassium carbonate for 20 hours. The ethyl derivative crystallised from alcohol as colourless needles melting at 116–7°, gave no colour with ferric chloride and was insoluble in aqueous alkali (Found: C, 70·2; H, 5·7; $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%.)

*Ethylation of prunetin to diethyl-prunetin:*

A sample of natural prunetin was ethylated with excess of ethyl iodide in acetone solution as described above. Prunetin diethyl ether crystallised from alcohol as colourless needles melting at 116–7°. It was identical in its properties with 7-methoxy-5:4′-diethoxy isoflavone (VI) and the mixed melting point was undepressed.

*2-Hydroxy-4:6-dimethoxy-phenyl-4′-methoxy-benzyl ketone (XVIII):*

2:4:6-Trihydroxy-phenyl-4′-methoxy-benzyl ketone[1] (4 g.) was refluxed in acetone solution with dimethyl sulphate (3 c.c.) and anhydrous potassium carbonate (6 g.) for 10 hours. Acetone was then distilled off and the residue treated with water and extracted with ether. The ether solution was extracted thrice with aqueous sodium hydroxide and the combined alkali extract was cooled and acidified. The colourless solid that separated out crystallised from alcohol in the form of colourless needles melting at 88–89° (see Robertson, *et al.*[12]). It gave a reddish brown colour with ferric chloride and a blue colour with concentrated nitric acid.

*5:7:4′-Trimethoxy isoflavone (genistein trimethyl ether) (XIX):*

Pulverised sodium (1 g.) was cooled in ice and treated with an ice-cold solution of the hydroxy-trimethoxy ketone (XVIII) in ethyl formate (10 c.c.) slowly with shaking. The mixture was left in the ice-chest for 48 hours

with occasional shaking. Pieces of ice were then added and ethyl formate removed under reduced pressure. The isoflavone that separated out was filtered and more of it was obtained by acidifying the aqueous solution. The combined product was washed with aqueous sodium hydroxide and crystallised from alcohol, when it separated in the form of colourless rectangular tablets melting at 160–61° identical with genistein trimethyl ether.[1, 2] Yield 1·2 g.

*Partial methylation of genistein to prunetin*:

Genistein (1 g.) was dissolved in dry acetone (100 c.c.), dimethyl sulphate (0·3 c.c., less than one mole) and anhydrous potassium carbonate (1 g.) added and the mixture refluxed for 4 hours. Acetone was then distilled off and the residue treated with water. The solid that separated out being insoluble in the carbonate solution was collected and washed with water. One crystallisation gave a product melting indefinitely between 210–20°. This was treated with 5% aqueous sodium hydroxide and the turbid solution filtered. On acidifying the alkaline solution a pale yellow solid was obtained (0·2 g.) which, after two crystallisations from alcohol came out as almost colourless needles melting at 238–40°. It gave a violet colour with ferric chloride and dissolved readily in aqueous sodium hydroxide. It agreed in its properties with prunetin and a mixed melting point with an authentic sample was undepressed. Acidification of the carbonate solution gave genistein (0·3 g.). (Found: C, 67·3; H, 4·4; $OCH_3$ 10·6; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2; $OCH_3$ 10·9%.)

The acetate prepared from the synthetic sample agreed with the derivative prepared from natural prunetin; m.p. and mixed m.p. 224–26°. The diethyl ether obtained by complete ethylation crystallised from alcohol as colourless needles and melted at 116–7° alone or in admixture with the synthetic 7-methoxy-5:4′-diethoxy isoflavone.

*Methylation of naringenin* (*sakuranetin*) (*XV*):

Naringenin (1 g.) was dissolved in acetone (30 c.c.), treated with dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (1 g.) and the mixture refluxed on a water-bath for 3 hours. Acetone was then distilled off and the residue treated with water. The solid that separated out being insoluble in aqueous potassium carbonate was filtered and crystallised from alcohol. The product melted at 98–100° even after two crystallisations. It was then treated with cold 2% aqueous sodium hydroxide and the turbid solution filtered. After cooling, the alkali solution was acidified with cold hydrochloric acid (1:1). The pale yellow solid that separated was filtered

and crystallised twice from aqueous alcohol when it was obtained as colourless prismatic needles melting at 152–4°. It agreed in all its properties with sakuranetin and a mixed melting point with a sample obtained from *Prunus puddum* was undepressed.

## Summary

The constitution of prunetin as the 7-methyl ether of genistein is established by preparing its diethyl ether and showing that it is identical with 7-methoxy-5:4′-diethoxy isoflavone obtained by independent synthesis. Prunetin itself has been synthesised by a method involving partial methylation of genistein using one mole of dimethyl sulphate. The theoretical considerations are discussed. The same procedure leads to a convenient preparation of sakuranetin.

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# STUDIES ON PLANT MUCILAGES

## Part II. Partial Hydrolysis of the Mucilage from the Tubers of *Asparagus filicinus*

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In the constitutional studies of gums and mucilages, partial or graded hydrolysis plays an important part. In several cases the change proceeds progressively, the component sugars getting detached one by one, and the final product is an aldobionic acid.

The mucilage from the tubers of *Asparagus filicinus* Buch.-Ham. *ex* D.Don, as already reported,[1] is composed of glucose, fructose, mannose and a uronic acid. With a view to obtaining a further knowledge regarding the mucilage molecule, it has been subjected to partial hydrolysis, as in the case of the mesquite gum,[2] by heatuing with 4 per cent. sulphuric acid at 80° for 3 hours. Amongst the products of hydrolysis, a polysaccharide and an aldobionic acid have been isolated.

The polysaccharide is composed of mannose, glucose and fructose in the molecular ratio of 9 : 8 : 2. It is soluble in water and also in 70 per cent. alcohol, and undergoes ready acetylation. The aldobionic acid undergoes further hydrolysis yielding mannose and glucuronic acid in equal proportion. It is, therefore, a manno-glucuronic acid. In this connection it may be noted that a manno-glucuronic acid (*β-d*-glucuronosido-2-*d*-mannose) was isolated from damson and cherry gums through partial hydrolysis,[3,4] and it remains to be seen whether these two aldobionic acids are identical or different.

From the results recorded above, it looks as though the mucilage molecule splits itself up into a manno-glucuronic acid and a polysaccharide. The latter still contains mannose, and hence it appears that a portion of the total mannose constituting the mucilage molecule is united to the uronic acid to form a resistant nucleus and the rest attached probably through different linkages.

### Experimental

*Partial Hydrolysis of the Mucilage.*—The mucilage (10 g.) was taken in a round bottom flask of 500 c.c. capacity and to it was added 4 per cent.

sulphuric acid (200 c.c.). The material almost immediately swelled into a thick dough, which was subsequently heated in a water-bath at 80° for 3 hours. As the heating progressed the contents became more and more fluid and after three hours they broke up into a thin colloidal solution and a coagulated precipitate. At this stage heating was stopped, the mixture cooled and filtered through a fine muslin. The filtrate was then passed through a fluted filter, when a clear solution was obtained. It was then neutralized with barium carbonate and concentrated to about 50 c.c. in an evaporating dish in the presence of barium carbonate. After filtration, the concentrate was cooled and treated with 95 per cent. alcohol (150 c.c.) when the barium salt of a complex uronic acid separated out. The barium salt and the sugar solution were treated separately.

The barium salt was purified by repeated dissolution in water and precipitation by means of alcohol. After the third precipitation, it was filtered, dehydrated using hot absolute alcohol and dried in a vacuum desiccator. On analysis it was found to contain 15·8 per cent. of barium (estimated as barium sulphate). On heating with 12 per cent. hydrochloric acid (method of Dickson, Otterson and Link for the estimation of uronic acid[5]) it liberated 4·64 per cent. of carbon dioxide. These data indicated that the substance was the barium salt of an aldobionic acid. (Barium aldobionate contains 16·21 per cent. of barium and liberates 5·19 per cent. of carbon dioxide).

The filtrate, left after the removal of barium aldobionate, was concentrated to about 30 c.c. by distillation under reduced pressure and then treated with 120 c.c. of alcohol, when a dark-coloured resinous mass separated out. The supernatant liquor, which contained some sugars, was decanted off, and the resinous residue, on trituration with hot methyl alcohol, became quite crisp. The solid was further purified by repeated precipitations from aqueous solutions by means of alcohol, till it attained a constant specific rotation. The product finally obtained was almost colourless with a pale yellowish tinge. It was amorphous under the microscope and did not melt below 250°. The substance responded to Dreywood reaction by developing a green colour, when treated with anthrone and sulphuric acid, thereby indicating its carbohydrate nature[6] (Found in a sample dried at 110° in vacuum: C, 43·91 and H, 5·82; $(C_6H_{10}O_5)_n$ requires C, 44·44 and H, 6·17%). The polysaccharide was freely soluble in water and aqueous alcohols up to 70 per cent. strength. Above this strength the solubility decreased gradually so that in alcohols of 90 per cent. strength and above the material was almost insoluble. In other organic solvents too it was insoluble. In 0·5 per cent. solution, its specific rotation $[\alpha]_D^{20°}$ was $-14·45°$. It reduced Fehling's solution, 100 mg. liberating 221·2 mg. of cuprous oxide.

The substance underwent ready acetylation when it was heated with acetic anhydride and anhydrous sodium acetate on a boiling water-bath for 6 hours. The acetyl derivative was freely soluble in chloroform and other organic solvents. However, on heating with hydroxy solvents, it used to undergo decomposition to some extent, probably through partial deacetylation. From chloroform solution it came out as an almost colourless substance with a slight yellow tinge and was found to be microcrystalline under the microscope. On heating it sintered at 165° and decomposed at about 180°. It contained 46·85 per cent. of $-COCH_3$. In chloroform solution its specific rotation was −15·0°.

*Hydrolysis of the Polysaccharide.*—The polysaccharide (2 g.) was disslolved in 4 per cent. sulphuric acid (100 c.c.) and mildly refluxed for 4 hours on a wire gauze. By this treatment the polysaccharide underwent complete hydrolysis. After neutralization with barium carbonate the hydrolysate was made upto 200 c.c. and analyzed for the constituent sugars. It was found to contain all the three sugars present in the original mucilage, namely, mannose, glucose and fructose. The presence of fructose was detected by its response to Pinoff's[7] and Seliwanoff's tests[8] and was confirmed by the formation of the characteristic osazone melting at 151°, when treated with methyl phenyl hydrazine according to the method of Bourquelot and Herissey[9]. The total sugars were estimated employing Fehling's solution and the total aldoses by the iodine-oxidation method of Willstätter and Schudel.[10] The difference between the total aldose content and that of mannose gave the amount of glucose, since these were the only two aldoses present. The balance of the sugars was obviously fructose. According to these estimations, mannose was found to be 47·4, glucose 42·1 and fructose 10·5 per cent., corresponding to 9, 8 and 2 molecules of mannose, glucose and fructose, respectively.

*Hydrolysis of the Aldobionic Acid.*—The barium salt of the aldobionic acid (1 g.) was dissolved in 20 c.c. of 2·5 N sulphuric acid and heated under reflux on a boiling water-bath for 20 hours. The small amount of the barium sulphate that separated as a result of the initial decomposition of the barium aldobionate did not interfere with the subsequent heating, and no attempt was, therefore, made to remove it. After the heating was over, the hydrolysate was neutralized with barium carbonate and filtered. The filtrate, when poured into alcohol, gave an insoluble barium salt (0·4 g.). It had $[\alpha]_D^{20°}$ + 13·8° (in water c=1); the specific rotation of barium glucuronate is reported to be +15·0° at 19°[11]. (Found: Ba, 25·6 per cent.; Barium glucuronate, Ba $(C_6H_9O_7)_2$, requires Ba, 26·3 per cent.). The barium salt, on oxidation

with nitric acid (1·15 d.) did not give any mucic acid, showing thereby that it was not derived from galacturonic acid.

The alcoholic filtrate from the barium glucuronate was distilled to remove all the alcohol. The aqueous solution on treatment with phenyl hydrazine in the cold very readily formed mannose phenyl hydrazone. No other sugars could be detected. The specific rotation of the sugar solution was 14·1°, indicating that it contained only mannose.

## Summary

The mucilage from the tubers of *Asparagus filicinus*, when subjected to partial hydrolysis by heating with 4 per cent. sulphuric acid at 80° for 3 hours, breaks into an aldobionic acid and a polysaccharide. The aldobionic acid is composed of mannose and glucuronic acid, while the polysaccharide is constituted from two molecules of fructose, eight molecules of glucose and nine of mannose.

The polysaccharide does not melt or decompose below 250° and has a specific rotation of −14·45°. It undergoes easy acetylation when treated with acetic anhydride and anhydrous sodium acetate. The acetyl derivative decomposes at about 180° and has a specific rotation of −15·0° in chloroform solution.

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# THERMAL EXPANSION OF CRYSTALS

## Part IV. Silver Chloride, Lithium Fluoride and Magnesium Oxide

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### 1. Introduction

In former parts of this series (Sharma, 1950) which appeared in these *Proceedings*, measurements on the thermal expansion of a few cubic crystals were reported. In continuation of this work, the author has now investigated the thermal expansion of three more cubic crystals, namely, silver chloride, lithium fluoride and magnesium oxide. The specimen of silver chloride was a special melt-grown polycrystalline mass in the form of a uniform sheet which was slightly coloured black superficially due to exposure to light. It was presented to Dr. G. N. Ramachandran by Baird Associates, Cambridge, Mass. The sample of LiF crystal was artificially grown and supplied by Harshaw Chemical Co., Ohio, U.S.A. MgO crystal was also synthetically grown and was lent by Sir C. V. Raman to whom the author's thanks are due. The crystals of LiF and MgO were not only perfectly clear and free from flaws, but were also practically all of a single crystal grain.

### 2. Previous Work

A survey of the literature has revealed that the only value for the thermal expansion of AgCl is that by Fizeau (1867) at 40° C. LiF has been investigated by Adenstedt (1936) in the low temperature region up to about −225° C., while above the room temperature it has been studied by Eucken and Dannöhl (1934) by employing an original heterodyne beat method. Periclase, the naturally occurring form of MgO, was studied by Fizeau (1867) at 40° C. and later by Goodwin and Mailey (1906) from 120° C. to 270° C. The first determination extending up to about 800° C. was undertaken by Merritt (1926) who made a comparative study with other refractory materials. However, no data are provided in his paper. Furthermore, the sample of magnesia used by him was taken from a fragment of used furnace lining and hence it was not pure, being 95% MgO with silica, lime, alumina and iron oxide as impurities. The first study on a pure sample of this crystal extending up to about 1,200° C. was made by Thilenius and Holzmann (1930) by using an optical dilatometric method. Their values are, however, slightly erratic and do not fall on a single smooth curve. The measurements

of Austin (1931), on the other hand, exhibit too great a discrepancy up to about 200° C. Durand (1936) has studied the thermal expansion of magnesium oxide in the low temperature region up to 85° K.

## 3. Results

In Tables I–III are contained the data for the coefficients of linear expansion at different temperatures for these crystals. In Tables IV and V are given the existing values of the coefficients of thermal expansion of LiF and MgO. The author's values inserted in these tables for comparison are calculated from the interpolation formula given for each crystal. From a perusal of Table IV it is seen that while Eucken and Dannöhl's values for LiF are in fair agreement up to about 400° C., the extrapolated values of the author

Table I. *Coefficient of thermal expansion for AgCl at different temperatures*

$\alpha_t = 0{\cdot}0_4 3136 - 0{\cdot}0_7 1588\ t + 0{\cdot}0_9 2038\ t^2$

| Temperature (° C.) | $\alpha \times 10^6$ (Observed) | $\alpha \times 10^6$ (Calculated) | Difference (%) |
|---|---|---|---|
| 42·5 | 31·05 | 31·05 | .. |
| 72·3 | 31·45 | 31·28 | +0·5 |
| 101·8 | 31·66 | 31·85 | −0·6 |
| 130·6 | 32·58 | 32·76 | −0·6 |
| 158·4 | 33·94 | 33·95 | .. |
| 184·9 | 35·73 | 35·39 | +1·0 |
| 210·2 | 37·11 | 37·02 | +0·2 |
| 234·4 | 38·95 | 38·83 | +0·3 |
| 262·8 | 41·49 | 41·26 | +0·6 |
| 295·0 | 44·10 | 44·40 | −0·7 |
| 325·0 | 47·74 | 47·73 | .. |

Table II. *Coefficient of thermal expansion for LiF at different temperatures*

$\alpha_t = 0{\cdot}0_4 3376 + 0{\cdot}0_7 2054\ t + 0{\cdot}0_{10} 4885\ t^2$

| Temperature (° C.) | $\alpha \times 10^6$ (Observed) | $\alpha \times 10^6$ (Calculated) | Difference (%) |
|---|---|---|---|
| 42·6 | 34·96 | 34·72 | +0·7 |
| 72·3 | 35·55 | 35·55 | .. |
| 101·3 | 36·41 | 36·34 | .. |
| 129·6 | 37·14 | 37·24 | −0·3 |
| 157·2 | 38·15 | 38·20 | .. |
| 184·0 | 39·27 | 39·19 | +0·2 |
| 210·0 | 40·42 | 40·22 | +0·5 |
| 235·4 | 41·07 | 41·30 | −0·6 |
| 260·3 | 42·04 | 42·42 | −0·9 |
| 284·4 | 43·76 | 43·55 | +0·5 |
| 313·4 | 44·99 | 44·99 | .. |
| 347·0 | 47·19 | 46·77 | +0·9 |
| 379·4 | 48·35 | 48·58 | −0·4 |

TABLE III. *Coefficient of expansion for MgO at different temperatures*

$$\alpha_t = 0{\cdot}0_4 1098 + 0{\cdot}0_8 5865\ t + 0{\cdot}0_{11} 1052\ t^2$$

| Temperature (° C.) | $\alpha \times 10^6$ (Observed) | $\alpha \times 10^6$ (Calculated) | Difference (%) |
|---|---|---|---|
| 50·3 | 11·28 | 11·28 | .. |
| 91·1 | 11·45 | 11·52 | −0·6 |
| 130·6 | 11·74 | 11·76 | .. |
| 168·7 | 12·09 | 12·00 | +0·8 |
| 205·6 | 12·39 | 12·23 | +1·3 |
| 241·5 | 12·58 | 12·46 | +1·0 |
| 276·9 | 12·73 | 12·69 | +0·3 |
| 311·7 | 12·88 | 12·90 | .. |
| 346·0 | 13·08 | 13·14 | −0·5 |
| 379·8 | 13·25 | 13·36 | −0·8 |
| 416·8 | 13·65 | 13·61 | +0·3 |
| 456·9 | 14·01 | 13·88 | +0·9 |
| 495·9 | 14·31 | 14·15 | +1·1 |
| 534·2 | 14·52 | 14·41 | +0·8 |
| 572·0 | 14·68 | 14·68 | .. |
| 609·4 | 14·82 | 14·95 | −0·9 |
| 646·2 | 15·14 | 15·21 | −0·5 |
| 682·2 | 15·46 | 15·47 | .. |
| 714·2 | 15·51 | 15·70 | −1·2 |

TABLE IV. *Comparative values of* $\alpha \times 10^6$ *for LiF*

| Temperature ° C. | 100 | 200 | 300 | 400 | 500 | 600 | 700 |
|---|---|---|---|---|---|---|---|
| Author | 36·30 | 39·82 | 44·32 | 49·79 | 56·24 | 63·67 | 72·08 |
| Eucken & Dannöhl | 36·48 | 40·28 | 44·55 | 49·31 | 54·55 | 60·26 | 66·46 |

TABLE V. *Comparative values of* $\alpha$ *for MgO*

| Temperature (° C.) | $\alpha \times 10^6$ (Literature) | $\alpha \times 10^6$ (Author) | Temperature (° C.) | $\alpha \times 10^6$ (Literature) | $\alpha \times 10^6$ (Author) |
|---|---|---|---|---|---|
| 40 | 10·43[1] | 11·22 | | | |
| 120–270 | 12·09[2] | 12·17 | 20–50 | 6·66 | 11·19 |
| 25–800 | 13·40[3] | 13·74 | 20–100 | 9·11 | 11·34 |
| 63·7 | 11·25 | 11·36 | | | |
| 153·0 | 11·90 | 11·90 | 20–150 | 10·38 | 11·49 |
| 246·3 | 12·82 | 12·49 | 20–200 | 10·88 | 11·65 |
| 348·2 | 13·77 [4] | 13·15 | 20–300 | 11·61 [5] | 11·97 |
| 448·4 | 14·12 | 13·80 | | | |
| 546·1 | 14·57 | 14·50 | 20–400 | 12·15 | 12·30 |
| 645·8 | 15·20 | 15·21 | 20–600 | 12·96 | 12·99 |
| 745·5 | 15·68 | 15·94 | 20–800 | 13·46 | 13·72 |

(1) Fizeau (1867); (2) Goodwin and Mailey (1906); (3) Merritt (1926); (4) Thilenius and Holzmann (1930); (5) Austin (1931).

at higher temperatures are greater than the values given by the former authors. In the case of MgO the agreement is fairly good in the low and high temperature regions; but the values of the author are consistently lower than those of Thilenius and Holzmann in the range 250°–450° C. Austin's values for MgO in the lower temperature region show too wide a divergence and appear to be erroneous.

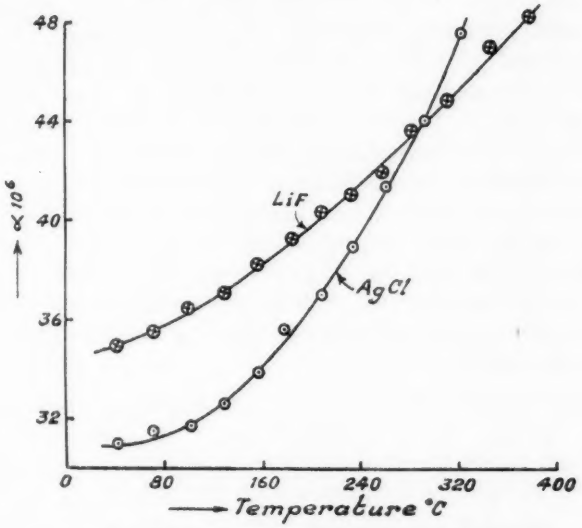


FIG. 1. Variation of α for AgCl and LiF with temperature

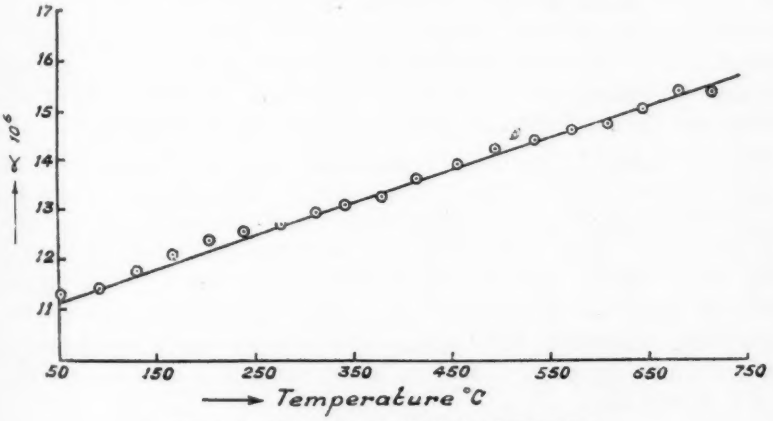


FIG. 2. Variation of α for MgO with temperature

The variation of the coefficient of linear expansion for AgCl and LiF is depicted graphically in Fig. 1, while that for MgO is represented in Fig. 2.

## 4. Discussion

From a comparative study of the values of the thermal expansion coefficients of the alkali halides one finds that although there is a remarkable gradation in their values, consistent with their other physical properties, the replacement of one ion in the lattice by another does not considerably alter the thermal expansion coefficient. Thus, for instance, the coefficient of expansion of LiF at 0° C. is $34 \times 10^{-6}$, that for NaCl is $40 \times 10^{-6}$, that for KBr is $38 \times 10^{-6}$ and that for AgCl which has the same lattice structure as that of rock-salt is $31 \times 10^{-6}$. The rate of variation with temperature of $\alpha$ for AgCl follows a course slightly different from that of the other alkali halides especially in the neighbourhood of the room temperature. When the temperature is lowered from 320° C., the $\alpha$-$t$ curve shows a steep fall up to about 160° C. below which the curve tends to flatten up. There is practically no variation of $\alpha$ in the range 100° to 20° C. The curve may be expected to exhibit another steep fall in the region of low temperatures. This is suggestive of some change taking place in the structure of AgCl in the neighbourhood of 0° C.

In the case of MgO which has the same lattice structure as rock-salt, one notices a striking difference in behaviour. The values of $\alpha$ for MgO at 0° C. and 800° C. are $10{\cdot}98 \times 10^{-6}$ and $16{\cdot}35 \times 10^{-6}$ respectively, while those for NaCl at the same temperatures are respectively $40{\cdot}31 \times 10^{-6}$ and $83{\cdot}62 \times 10^{-6}$. Not only the absolute value of $\alpha$ for MgO at any temperature is much less than that of NaCl, but its rate of variation with temperature is also much smaller. Although the interpolation formula given above for MgO is parabolic in form, yet the last term is so small that its contribution to $\alpha$ up to the temperature investigated in this case is not very preponderant. Hence the $\alpha$-$t$ curve for MgO follows more a linear relationship than the parabolic one, as the curve in Fig. 2 indicates.

The low value of $\alpha$ for MgO is consistent with the bivalent nature of the ions involved in the lattice. Since each ion in a divalent crystal has twice as great a charge as in a similar monovalent one, the interionic forces are four times as great. Moreover, the interionic separation in NaCl is 2·81 Å, while that in MgO is only 2·10 Å (Slater, 1939). These factors result in the higher elastic constants and consequently lower compressibility for the latter. Moreover, MgO has a correspondingly large latent heat of fusion and its melting point (2,800° C.) is also many times greater than that (804° C.) of rock-salt.

## 5. Evaluation of Grüneisen's Constant

*AgCl.*—For evaluating the Grüneisen's constant, the values of which are entered in Table VI the $C_p$ values are calculated from equation (1) given by Kelley (1934), which is based on the experimental results of Ehrhardt (1885), Goodwin and Kalmus (1909) and Magnus (1910).

$$C_p = 9{\cdot}60 + 9{\cdot}29 \times 10^{-3}T. \qquad (1)$$

The value of compressibility ($2{\cdot}45 \times 10^{-12}$ cm.$^2$/dyne) has been taken from Richards and Jones (1909).

Table VI. *Grüneisen's constant for AgCl at different temperatures*

| Temperature (°C.) | $C_p$ (Cals. deg.$^{-1}$ mol.$^{-1}$) | $C_v$ (Cals. deg.$^{-1}$ mol.$^{-1}$) | $\alpha \times 10^6$ (deg.$^{-1}$) | $\gamma$ |
|---|---|---|---|---|
| 40 | 12·51 | 11·82 | 31·05 | 1·97 |
| 80 | 12·88 | 12·06 | 31·39 | 1·96 |
| 120 | 13·25 | 12·29 | 32·39 | 1·98 |
| 160 | 13·62 | 12·50 | 34·04 | 2·05 |
| 200 | 13·99 | 12·69 | 36·31 | 2·15 |
| 240 | 14·37 | 12·89 | 39·29 | 2·29 |
| 280 | 14·74 | 13·06 | 42·89 | 2·47 |
| 320 | 15·11 | 13·22 | 47·14 | 2·68 |

*LiF.*—Specific heats are calculated from equation (2) also given by Kelley (1934). The compressibility at absolute zero of temperature and under no

Table VII. *Grüneisen's constant for LiF at different temperatures*

| Temperature (° C.) | $C_p$ (Cals. deg.$^{-1}$ mol.$^{-1}$) | $C_v$ (Cals. deg.$^{-1}$ mol.$^{-1}$) | $\alpha \times 10^6$ (deg.$^{-1}$) | $\gamma$ |
|---|---|---|---|---|
| −222·1 | .. | 0·49 | 1·52 | 1·57 |
| −180·0 | .. | 2·62 | 8·40 | 1·63 |
| −103·6 | .. | 6·52 | 22·36 | 1·75 |
| − 41·3 | .. | 8·36 | 29·07 | 1·77 |
| +100 | 10·14 | 9·48 | 36·30 | 1·95 |
| 200 | 10·66 | 9·73 | 39·82 | 2·08 |
| 300 | 11·18 | 9·94 | 44·32 | 2·27 |
| 400 | 11·70 | 10·11 | 49·79 | 2·51 |

external pressure has been given by Slater (1924) and this value ($1 \cdot 40 \times 10^{-11}$ cm.$^2$/dyne) has been employed in the present calculations. The $\gamma$ values are tabulated in Table VII.

$$C_p = 8 \cdot 20 + 5 \cdot 20 \times 10^{-3} T \qquad (2)$$

For evaluating the Grüneisen's constant for this salt in the low temperature region the values of $\alpha$ have been taken from Adenstedt (1936) while $C_v$ values are taken from Clusius's paper (1946).

In both cases, the Grüneisen's constant $\gamma$ exhibits a marked variation with temperature.

In conclusion, the author takes this opportunity to thank Professor R. S. Krishnan for his keen interest in this work.

## Summary

By employing the interferometric method, the temperature variation of thermal expansion of AgCl, LiF and MgO crystals has been studied up to 325° C., 380° C. and 710° C. respectively. The coefficient of expansion has been calculated for each crystal and has been correlated with temperature by an interpolation formula of the parabolic type. Grüneisen's constant has been calculated for AgCl above the room temperature and for LiF from −222° C. to 400° C. and is found to vary markedly with temperature in both cases.

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# ELASTIC CONSTANTS OF ORTHORHOMBIC SULPHUR

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Received September 4, 1950

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

## 1. Introduction

As is well known, the most stable form of crystalline sulphur at room temperature is the so-called $\alpha$-variety, belonging to the orthorhombic system. Besides being one of the few elements which occur in pure crystalline form and readily obtained form solutions in carbon disulphide, etc., it has many interesting properties. If the crystals are grown out of molten sulphur, the $\beta$- or the monoclinic variety occurs and it gradually changes over to the more stable $\alpha$ variety on standing at room temperature. Many of its properties have been extensively studied by a number of workers.

Concerning the investigations of the elastic properties, however, only the compressibility of the orthorhombic sulphur was studied by Richards (1927) Madelung and Fuchs (1935) and Bridgman (1927). Hence, it was proposed to determine all the nine separate constants of the crystal and the results are given in the following sections.

## 2. Growth of Crystals and Preparation of Sections

Very good single crystals of orthorhombic sulphur can be grown from solutions in carbon disulphide, chloroform, chlorobenzene or bromobenzene by carefully regulating the rate of evaporation of the solution. In the present study carbon disulphide solutions were used. A few words about the method of growing crystals from carbon disulphide solutions are, however, necessary. In the first place, saturated solutions should be avoided and are in fact not necessary. The solution should be sufficiently dilute and kept in an almost air tight dessicator. The size of the crystallizing dish or specifically the ratio of the height of the solution to the area of the surface exposed was found to have a marked influence on the growth of

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good single crystals. Thus, if the surface was either too small or too large, sulphur precipitated as a shower of tiny crystals; and the same was the case with saturated solutions also. The best size of the dish was found to be about 2″ to 2·5″. The dish should be absolutely dry and free from sulphur dust. A few shavings of paraffin wax were placed in the dessicator to absorb the carbon disulphide vapour. Good transparent crystals of the size 1 to 2 c.c. were grown in the above manner.

Forms that are chiefly obtained are many. The following data given by Groth have been used to identify the faces:—

$$a:b:c = 0{\cdot}8108:1:1{\cdot}9005$$

$$p:p = (111):(1\bar{1}1) = 73°\,32'$$

$$p:p = (111):(\bar{1}11) = 94°\,57\tfrac{1}{2}'$$

$$p:p = (111):(11\bar{1}) = 36°\,46'$$

Grown out of $CS_2$ solutions, the author could rarely get any faces other than the *p*. With the help of the above data, the faces were identified and the necessary sections were cut and ground to uniform thickness. Ordinary methods of cutting with a wet thread or copper wire, etc., are absolutely unsuitable since the crystal is very brittle and extremely heat sensitive. Abrasives cannot also be used for the same reason. The best way of preparing the sections was, however, found to be that of erasing the crystal with the sharp edge of a razor blade and then grinding it gently on a slightly ground-glass plate.

As usual, the $X_1$-, $X_2$-, $X_3$-cuts were used to give the six constants of the type $C_{ii}$ and three more sections with their normals lying in the axial planes, equally inclined to the two concerned axes were used to determine the remaining three constants of the type $C_{ij}$ $(i \neq j)$.

The details of the rigorous calculations for the orthorhombic system are the same as those given in a previous publication by the author (Sundara Rao, 1950).

The experimental technique used was the usual ultrasonic method using Debye–Sear's pattern: A saturated solution of sulphur in toluene was used as the liquid in which the pattern was observed since toluene dissolved sulphur to a slight extent.

## 3. Experimental Data and Results

The relevant experimental data are given in Table I.

TABLE I

Density = 2·07 gm. cm.$^{-3}$ Unit = $10^{11}$ dynes/cm.$^2$

| No. | Description of the plate | Thickness in mm. | Frequency Mc./Sec. | Mode | Type of the constant | Value of the constant |
|---|---|---|---|---|---|---|
| 1 | $X_1$-Cut | 1·00 | 1·716 | (1) | $C_{11}$ | 2·398 |
| 1 | ,, | ,, | 0·9715 | (*t*) | $C_{66}$ | 0·7686 |
| 1 | ,, | ,, | 1·035 | (*t*) | $C_{55}$ | 0·8724 |
| 2 | $X_2$-Cut | 0·835 | 1·884 | (1) | $C_{22}$ | 2·047 |
| 2 | ,, | ,, | 0·8607 | (*t*) | $C_{44}$ | 0·4279 |
| 2 | ,, | ,, | 1·139 | (*t*) | $C_{66}$ | 0·7498 |
| 3 | $X_3$-Cut | 1·12 | 2·156 | (1) | $C_{33}$ | 4·827 |
| 3 | ,, | ,, | 0·9165 | (*t*) | $C_{55}$ | 0·8724 |
| 3 | ,, | ,, | 0·643 | (*t*) | $C_{44}$ | 0·4294 |
| 4 | $X_1$ 45$X_2$ | 1·805 | 1·166 | (1) | $X_1$ | 3·670 |
| 5 | $X_2$ 45$X_3$ | 1·100 | 1·768 | (1) | $X_1$ | 3·132 |
| 6 | $X_5$ 45$X_1$ | 1·1525 | 1·148 | (1) | $X_1$ | 2·537 |

Using the above data and the method of calculations explained in a prevoius publication (Sundara Rao, 1950) the following constants are obtained in units of $10^{11}$ dyes/cm.$^2$

$$C_{11} = 2{\cdot}40 \quad C_{44} = 0{\cdot}43 \quad C_{23} = 1{\cdot}59$$

$$C_{22} = 2{\cdot}05 \quad C_{55} = 0{\cdot}87 \quad C_{31} = 1{\cdot}71$$

$$C_{33} = 4{\cdot}83 \quad C_{66} = 0{\cdot}76 \quad C_{12} = 1{\cdot}33$$

The elastic moduli $s_{ij}$ are also calculated and given below in units of $10^{-13}$ cm.$^2$/dyne.

$$s_{11} = 89{\cdot}9, \quad s_{44} = 232, \quad s_{12} = 45{\cdot}2$$

$$s_{22} = 106{\cdot}0, \quad s_{55} = 115, \quad s_{13} = 13{\cdot}6$$

$$s_{33} = 38{\cdot}4, \quad s_{66} = 132, \quad s_{23} = 18{\cdot}8$$

The author expresses his grateful thanks to Professor R. S. Krishnan for his kind interest and guidance in the work.

## 4. Summary

The elastic constants of single crystals of orthorhomibc sulphur have been determined by ultrasonic method. The values in units of $10^{11}$ dynes/cm.$^2$ are

$C_{11} = 2 \cdot 40$ $C_{44} = 0 \cdot 43$ $C_{31} = 1 \cdot 59$

$C_{22} = 2 \cdot 05$ $C_{55} = 0 \cdot 87$ $C_{23} = 1 \cdot 71$

$C_{33} = 4 \cdot 83$ $C_{66} = 0 \cdot 76$ $C_{12} = 1 \cdot 33$


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# RAMAN SPECTRUM OF RUTILE ($TiO_2$)

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Received July 4, 1950

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

## 1. Introduction

Rutile has a simple structure characteristic of compounds of the type $AB_2$ in which the A atom has a co-ordination number 6, and a study of its Raman spectrum is therefore of special interest. A large boule of synthetic rutile and a smaller cut stone were placed at the disposal of the author by Professor C. V. Raman and enabled a study of its Raman spectrum to be made. The results are described below.

## 2. Experimental Results

As the specimen used in the present investigation was coloured slightly yellow, only the visible radiations of the mercury arc could be used for exciting the Raman spectrum. However, as the refractive index of rutile is known to be unusually high (2·9), it is natural to expect the scattering to be very intense. A Hilger two prism spectrograph of high light gathering power and with a dispersion of 140 $cm.^{-1}$ in the $\lambda$ 4358 region was used and the slit-width employed in the preliminary exposures was 0·15 mm. It was noticed that even with a much smaller (cut) specimen, exposures of the order of 8 hours were sufficient to bring out the main features of the spectrum, while with the larger specimen which was in the form of a boule $1\frac{1}{4}''$ long intense pictures were obtained in 3 days. The frequency shifts and the nature of the Raman lines observed are given in Table I.

The Raman lines excited by $\lambda$ 5461 line of mercury were of considerably greater intensity, owing to the slightly yellowish colouration of the crystal. But as a spectrograph with a large dispersion in the green region was not available, the author was unable to make use of the above observation.

The Raman spectrum of rutile reveals some very interesting features. In addition to the five intense lines at 236, 440, 515, 589 and 650 $cm.^{-1}$, there are two broad bands 350–420 $cm.^{-1}$ and 1,000–1,200 $cm.^{-1}$. The former shows some structure. In the reproduced microphotometer record (see Fig. 1), the lines appear to be unusually broad, mainly due to the width of the slit employed in recording them.

TABLE I

| Mode | Frequency shift in cm.$^{-1}$ | Intensity | Nature of the line |
|---|---|---|---|
| – | 150 | 0 | – |
| $B_{1g}$ | 236 | 5 | Broad and diffuse |
| $A_{2u}$ | (Infra-red) 333 | | |
| $E_g$ | 300–440 | 6 | Broad |
| $A_{1g}$ | 440 | 10 | Sharp |
| – | 515 | 3 | ,, |
| $B_{2g}$ | 589 | 7 | ,, |
| – | 650 | 3 | ,, |
| – | 1,000–1,200 | 1 | – |

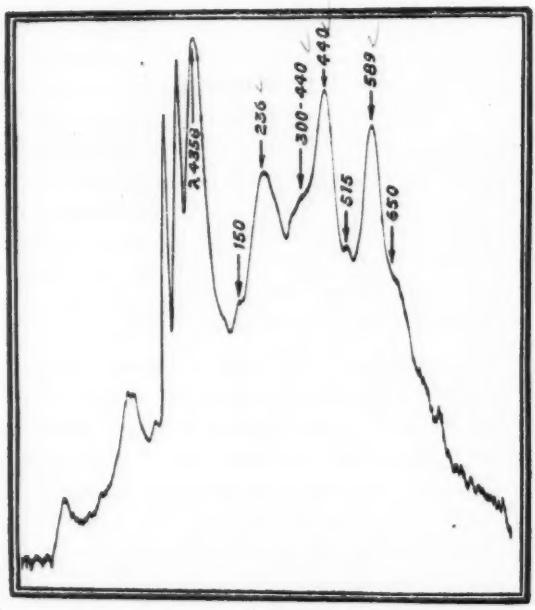


FIG. 1. Microphotometer Curve of the Raman Spectrum of Rutile.

## 3. Discussion

The crystal structure of rutile, which is isomorphous with casseterite ($SnO_2$) is essentially very simple and has been determined by L. Vegard (1916). It is based on a tetragonal lattice with the space group $D^{14}_{4h}$ and the unit cell contains 2 molecules. Fig. 2 represents the projection of the unit cell on the basal plane (001). The titanium atoms are at the corners

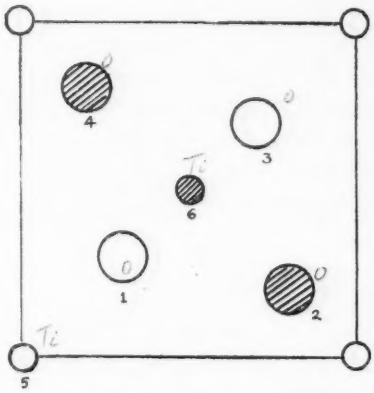


Fig. 2. Raman Spectrum of Rutile

and centres of the cells, while the oxygen atoms lie on the base diagonals and at similar positions half-way up the cell with the co-ordinates given below.

$T_i$ atoms (5, 6) 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$;

O atoms (1, 2, 3, 4) $uuo$; $\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}$; $\bar{u}\bar{u}o$; $\frac{1}{2}-u, \frac{1}{2}+u, \frac{1}{2}$;

with the parameter $u = 0{\cdot}31$

The operations of the group may be expressed as follows:

| | |
|---|---|
| E | (Identity) |
| $2C_4^s$ | (4123) (65)<br>(1432) (56) |
| $C_2''$ | (13) (24) (5) (6) |
| $2C_2^s$ | (12) (34) (56)<br>(14) (23) (56) |
| $2C_2'$ | (13) (5) (56)<br>(5) (1) (6) (3) (24) |

$\sigma_h$ (1) (2) (3) (4) (5) (6)

$2\sigma^g$ {(56) (12) (3 4)
{(5 6) (1 4) (2 3)

$2\sigma_v'$ {(5) (6) (4) (2) (13)
{(5) (6) (1) (3) (24)

$2S_4$ {(1432) (56)
{(4132) (65)

i (5) (6) (24) (13)

By the application of the group theoretical methods to the Bravais cell of smallest size, it is possible to obtain useful information concerning the $(3p - 3)$ internal oscillations of the $p$ non-equivalent atoms in the unit cell. The character table and other relevant features are given in Table II.

TABLE II

| $D_{4h}$ | E | $2C_4$ | $C_2''$ | $2C_2$ | $2C_2'$ | $\sigma_h$ | $2\sigma_v$ | $2\sigma_v'$ | $2S_4$ | $i$ | $n_i$ | T | $n_i'$ | Raman | Infra-red |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_{1g}$ .. | +1 | +1 | +1 | +1 | +1 | +1 | +1 | +1 | +1 | +1 | 1 | 0 | 1 | p | f |
| $A_{1u}$ .. | +1 | +1 | +1 | +1 | −1 | −1 | −1 | −1 | −1 | −1 | 0 | 0 | 0 | − | − |
| $A_{2g}$ .. | +1 | +1 | −1 | −1 | −1 | −1 | −1 | −1 | +1 | +1 | 1 | 0 | 1 | f | f |
| $A_{2u}$ .. | +1 | +1 | +1 | −1 | −1 | −1 | +1 | +1 | −1 | −1 | 2 | 1 | 1 | f | $M_z$ |
| $B_{1g}$ .. | +1 | −1 | +1 | +1 | −1 | +1 | +1 | −1 | −1 | +1 | 1 | 0 | 1 | p | f |
| $B_{1u}$ .. | +1 | −1 | +1 | +1 | −1 | −1 | −1 | −1 | +1 | −1 | 2 | 0 | 2 | f | f |
| $B_{2g}$ .. | +1 | −1 | +1 | −1 | +1 | +1 | −1 | +1 | −1 | +1 | 1 | 0 | 1 | p | f |
| $B_{2u}$ .. | +1 | −1 | +1 | −1 | +1 | −1 | +1 | −1 | +1 | −1 | 0 | 0 | 0 | f | f |
| $E_g$ .. | +2 | 0 | −2 | 0 | 0 | 2 | 0 | 0 | 0 | +2 | 1 | 0 | 1 | p | f |
| $E_u$ .. | +2 | 0 | −2 | 0 | 0 | +2 | 0 | 0 | 0 | −2 | 4 | 1 | 3 | f | $M_x$ |
| $U_R$ .. | 6 | 0 | 2 | 0 | 4 | 6 | 0 | 4 | 0 | 2 | | | | | |
| $\chi_\rho(R)$ | 18 | 0 | −2 | 0 | −8 | 6 | 0 | 8 | 0 | −6 | | | | | |

We see from the table that the 15 modes fall under 8 representations of which 4 are allowed in the Raman effect and 4 in the infra-red. As a centre of inversion is one of the elements in the group, the infra-red maxima and Raman shifts are complementary. Modes $A_{1g}$ and $B_{2g}$ are both symmetric with respect to the centre of synmmetry and differ in respect to their behaviour towards the fourfold screw axis. In both these modes, the Ti

atoms are at rest. In the symmetric vibration, atoms 1 and 3 move towards each other and 2 and 4 move out, while in the other mode the two pairs move in or out in phase. Obviously we can expect the vibration $B_{2g}$ to have the higher frequency.

The third non-degenerate vibration allowed in Raman effect is one in which the Ti atoms are at rest and the O atoms move tangentially with respect to the bond Ti — O and as such is likely to show a large amount of thermal broadening. The broad line at 230 cm.$^{-1}$ may be assigned to this mode and a study of the spectrum at a low temperature may be expected to confirm this assignment. Table I gives the assignment of the Raman lines from a consideration of their activity in the infra-red and Raman effect and their relative intensities.

The infra-red rest-strahlen maxima, as reported by Liebisch and H Rubens, are:

| | | | | |
|---|---|---|---|---|
| Ordinary ray | $14{\cdot}5\mu$ | $16\mu$ | $18{\cdot}5\mu$ | $39\mu$ |
| Extra-ordinary ray | $16\mu$ | $19{\cdot}3\mu$ | $22{\cdot}2\mu$ | $30\mu$ |

It is believed that the maxima $16\mu$, $18{\cdot}5\mu$ and $19{\cdot}3\mu$ are due to the degenerate modes $E_u$ in which the atomic displacements are perpendicular to the C axis, though for a definite assignment of these as well as the maxima at $14{\cdot}5\mu$, $39\mu$ and $22{\cdot}2\mu$ a theoretical evaluation of the frequencies of vibration is essential. The Raman line at 515 cm.$^{-1}$ is probably due to the same mode as the infra-red maxima in the neighbourhood of $19\mu$ though according to selection rules, it is not permitted in Raman scattering. As in diamond, the enormous scattering power results in the appearance of the second-order spectrum as a broad band from 1,000–1,200 cm.$^{-1}$.

The author is indebted to Professor C. V. Raman for a loan of the specimens used in this investigation and to Professor R. S. Krishnan for his guidance in the course of the work.

## Summary

The Raman spectrum of rutile ($TiO_2$) has been recorded using the visible radiations of the mercury arc. The 8 observed Raman lines have been partially explained on the basis of an elementary group-theoretical analysis.

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